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# Polonium-210 dynamics in the northern Gulf of Mexico

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# POLONIUM-210 DYNAMICS IN THE NORTHERN GULF OF MEXICO

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# ABSTRACT

$^{210}$Po ($t_{1/2}$=138 d) is the most common among the 33 known radioisotopes of Polonium found in the natural environment. It is produced by the radioactive decay of its long-lived grandparent $^{210}$Pb ($t_{1/2}$=22.3 d) via $^{210}$Bi ($t_{1/2}$=5.012 d) and forms as part of the natural $^{238}$U decay series. Polonium has been known to bioaccumulate in the marine food web and can be potentially harmful to humans via the intake of certain marine organisms. Thus it is important to understand the source and sink of $^{210}$Po in the marine environment. Studies in the past have observed $^{210}$Po remobilization from sediments in anoxic lake environments but this has never been studied in low oxygen marine systems. The present work is aimed at understanding both remobilization of $^{210}$Po from sediments in the hypoxia zone of the northern Gulf of Mexico and utilizing $^{210}$Po as a tracer of POC export in the northern Gulf of Mexico.

Results from the first study indicate $^{210}$Po was enriched in bottom waters by as much as 50% compared to surface waters from sample stations in the hypoxia zone in 2011 and 2012. There was a good correlation between $^{210}$Po enrichment and the release of redox sensitive trace metals like Fe and Mn. The cycling of redox sensitive elements such as Fe and Mn and the degradation of organic matter in the water column are likely the driving mechanisms of $^{210}$Po remobilization from sediments to the water column under hypoxic conditions.

The second study utilized $^{210}$Po as a tracer for POC export in the Gulf of Mexico. POC fluxes were estimated using the $^{210}$Pb – $^{210}$Po disequilibria in the water column and varied between 10.4 mg C $m^{-2}$ $d^{-1}$ and 85.6 mg C $m^{-2}$ $d^{-1}$ and showed a general

decreasing trend further offshore similar to the decrease in net primary productivity further from shore. The efficiency of the biological pump was found to decrease from 21% at stations close to shore to 4% at stations further offshore, suggesting a transition in POC export efficiency from nutrient rich eutrophic water to nutrient poor oligotrophic water.

# CHAPTER 1: INTRODUCTION

Marie and Pierre Curie discovered polonium in 1898. It was tentatively named "Radium F" but later renamed after Marie Curie's native land of Poland. The element was the first one discovered by the Curies while they were investigating the cause of pitchblende radioactivity. The pitchblende, after removal of the radioactive elements uranium and thorium, was more radioactive than both the uranium and thorium put together (http://education.jlab.org). This motivated the Curies to explore additional radioactive elements and they first separated polonium from the pitchblende in July 1898. Polonium is a member of the naturally occurring $^{238}U$ decay-chain and has 33 known isotopes, all of which are radioactive.

$^{210}Po$ ($t_{1/2}$ = 138.376 d) is the most common in the natural environment and is the product of $^{210}Pb$ ($t_{1/2}$ = 22.3 y) decay via the short-lived intermediate daughter $^{210}Bi$ ($t_{1/2}$ = 5.013 d). Polonium and other radioisotopes in the $^{238}U$ decay-series have been utilized for various purposes such as dating archeological material, catalysts in modern medicine, tracers of geochemical processes, etc. (http://education.jlab.org). Most of the members of this decay-series are characterized by short half-lives and unique particle affinities, which allows for the study of specific geochemical and geophysical processes. For example, quantifying the disequilibria of $^{238}U$-$^{234}Th$ or that of $^{210}Pb$-$^{210}Po$ in the water column can provide insight on the carbon flux in the open ocean due to polonium and thorium's affinity for biological material.

$^{210}Po$ is primarily an alpha emitter. It decays directly to its daughter isotope, stable $^{206}Pb$. $^{210}Po$ is considered extremely radioactive, in fact a milligram of $^{210}Po$ emits about as many alpha particles per second as 5 grams of $^{226}Ra$

(http://education.jlab.org). Due to its ionization potential, alpha particle emission is the most dangerous form of radioactive decay to living organisms and has been associated with carcinogenic side effects. Polonium has no known natural compounds, only synthetically created ones, of which more than 50 are known (http://education.jlab.org). The chemistry of polonium is similar to that of tellurium and bismuth and it dissolves readily in dilute acids, but is only slightly soluble in alkalis. Polonium is an extremely rare element in nature because of the short half-life associated with all of its isotopes. It is commonly found in uranium ores at about 0.1 mg per metric ton, approximately 0.2% of the abundance of radium. The amounts in the Earth's crust are not harmful, unless concentrated via remobilization or a similar process. The highest dose of $^{210}$Po that humans typically encounter in everyday life is likely from tobacco smoke as high activities of Polonium have been detected in tobacco smoke from tobacco leaves grown with phosphate fertilizers (http://education.jlab.org).

## 1.1 The Natural $^{238}$U Decay Chain and Sources of Polonium

The Uranium decay chain is a naturally occurring decay sequence of radioisotopes that are produced as a result of alpha, beta, and gamma emission. This decay series terminates with the production of the stable $^{206}$Pb isotope. Due to their particle affinities and geochemical applications, $^{210}$Po and $^{210}$Pb are especially significant members of the $^{238}$U decay chain. $^{210}$Po forms via the decay (primarily beta emission) of $^{210}$Pb. There is a short-lived intermediate daughter that is produced before $^{210}$Po, the $^{210}$Bi ($t_{1/2}$ = 5.012 d) radioisotope. $^{210}$Po is the final radioactive daughter of the $^{238}$U chain and decays directly to the final overall member, stable $^{206}$Pb via alpha emission. $^{210}$Pb and $^{210}$Po activities in the natural environment can reveal valuable

information about the rates of transfer of different chemical species between particulate and dissolved phase, particle residence times, and sedimentation rates. $^{210}$Pb is highly particle reactive and because of its long-lived half-life, it is utilized to study sedimentation rates in coastal and open ocean environments. $^{210}$Po is also particle reactive and has a higher affinity for biological material, which can reveal valuable information about the marine food web and the particulate organic carbon flux in the open ocean.

Several sources of these radioisotopes exist naturally in the environment. The primary source of $^{210}$Pb and $^{210}$Po in the environment is the exhalation of $^{222}$Rn ($t_{1/2}$ = 3.8 d) from continents into the atmosphere. $^{222}$Rn, also a radioactive member of the $^{238}$U decay chain, is released as a gas from continental rock into the atmosphere. $^{210}$Po that is produced from $^{210}$Pb is negligible in precipitation from the atmosphere because of the short residence time of aerosols in the atmosphere. Therefore, most of the $^{210}$Po in the aqueous environment is related to in situ decay of $^{210}$Pb within sediments. Other than atmospheric input, polonium in the water column can also result from in situ decay of $^{226}$Ra. This could be an important source in coastal environments where sediments are enriched in $^{226}$Ra ($t_{1/2}$ = 1620 y) or are receiving a large volume of submarine groundwater discharge enriched in $^{210}$Po (Harada et al., 1988).

## 1.2 Polonium Biogeochemistry

$^{210}$Pb quickly absorbs to all sedimentary particle surfaces. $^{210}$Po, however, becomes incorporated via biological activity into the cytoplasm and cell wall of some species of phytoplankton (Fisher et al., 1983). The partitioning of $^{210}$Po is thought to be similar to that of protein and sulfur within the cell (Fisher et al, 1983; Stewart and Fisher,

2003a, 2003b). The biogeochemical differences between $^{210}$Pb and $^{210}$Po result in $^{210}$Po being more efficiently removed from surface waters than $^{210}$Pb via the scavenging by sinking particles. The relative deficiency of $^{210}$Po with respect to its parent $^{210}$Pb in the euphotic zone is often used to trace organic carbon export from the upper water column in the open ocean. Higher trophic level organisms such as marine copepods also indicate a relatively high assimilation efficiency of $^{210}$Po by zooplankton (Stewart and Fisher, 2003b). The high assimilation efficiency coupled with slow loss rate make zooplankton effective conduits for the transfer to higher trophic levels and bioaccumulation in the marine food web, potentially contaminating seafood. This enrichment among higher trophic levels in the marine environment is mainly due to the uptake of food rather than directly from intake of seawater (Kim et al., 2005). $^{210}$Po has been found to concentrate in the hepatopancreas of several marine invertebrates; several studies have shown $^{210}$Po to be associated with protein in this organ (Fisher et al., 1983).

There is also evidence that two pools of $^{210}$Po are associated within cells: a surface-bound pool and an internal pool. The polonium in the internal pool's association with cytoplasm and protein is what results in the efficient assimilation of $^{210}$Po by phytoplankton (Stewart and Fisher, 2003a; Reinfelder and Fisher, 1991). This ultimately leads to bioconcentration in the marine food web. The external pool, in contrast, could be expected to behave more like other surface-bound particle-reactive radionuclides such as $^{210}$Pb and $^{234}$Th, which are not assimilated in animal tissue and sink in fecal material (Fisher and Reinfelder, 1995). Inside the cell however, $^{210}$Po is associated with proteins and sulfur-containing compounds within bacterial cells, phytoplankton and

zooplankton (Fisher et al., 1983). This suggests that polonium may be a class B, sulfur-seeking metal (Nieboer and Richardson, 1980). Ultimately, we would expect polonium to be highly correlated with sulfur, protein, or other sulfur-seeking metals in the natural environment.

There have been many studies to trace particle fluxes using radioisotopes such as $^{210}$Pb and $^{210}$Po but few have attempted to understand which component of particle influence the activity of radioisotope, $^{210}$Pb or $^{210}$Po. $^{210}$Po has been shown to correlate with particulate organic carbon (POC), while $^{210}$Pb and $^{234}$Th activities correlate with both POC and biogenic silica in the Southern Ocean (Friedrich and van der Loeff, 2002). It is also important to note that proteinaceous material makes up a major fraction of particulate organic matter in the ocean (Lee et al., 2000). A study done by Stewart et al. in 2007 that utilized radioactive tracers to observe the behavior and composition of sinking particles indicate that $^{210}$Po may help better track the organic and carbon fraction of sinking particles.

## 1.3 Polonium Dynamics in the Natural Environment

### 1.3.1 Polonium Remobilization from Anoxic Sediments

The majority of recent studies involving the environmental implications of polonium contamination have addressed the remobilization of $^{210}$Po from anoxic lake sediments. One study done by Benoit and Hemond (1990) analyzed the remobilizing potential of $^{210}$Pb and $^{210}$Po in anoxic lake sediments. Their results indicate that $^{210}$Po is released into suboxic waters from sediment resulting in unsupported $^{210}$Po. $^{210}$Po cycling is thought to parallel the redox characteristics of Mn in that both are released in substantial amounts to bottom water that contain low levels of dissolved oxygen and are

highly sensitive to redox conditions. However, it is difficult to establish with certainty the possibility that $^{210}$Po release correlates with Mn rather than Fe because both Mn and Fe release correlate well with each other. There are currently no published data sets addressing the remobilization potential of $^{210}$Po in coastal waters, such as the Gulf of Mexico hypoxia zone.

After three decades of scientific study utilizing $^{210}$Po and $^{210}$Pb in the marine environment, large uncertainties remain regarding our understanding of oceanic geochemistry of these two nuclides, especially polonium. Even though the speciation chemistry of Po in seawater is largely speculative (Harada et al, 1989; Benoit and Hemond, 1990), thermodynamic considerations predict that in well-oxygenated pH neutral waters, aqueous Po should exist predominately as tetravalent $PoO_2$, and while under reducing conditions a divalent species should exist. It has been suggested that Po(IV) is insoluble and is reduced to Po(II) similar to the potential of Mn(IV) reduction to Mn(II) (Benoit and Hemond, 1990; Balisterieri et al., 1995). Redox sensitive elements such as, S, Fe, and Mn appear to diffuse to bottom waters from sediments under anoxic conditions by forming reduced soluble species. In contrast Fe and Mn oxides/hydroxides that precipitate under oxic conditions may serve as an effective carrier of Po in aqueous environments.

The remobilization of $^{210}$Po into partially oxygen-depleted waters has been documented in several studies from lacustrine environments. While Po in most natural waters is particle reactive, one study has shown that it can exist in a more soluble form in low oxygen environments (Kim et al., 2005). The cycling of $^{210}$Po in waters from a seasonally anoxic pond in South Carolina showed an excess of $^{210}$Po with respect to its

parent $^{210}$Pb for both summer and winter (Kim et al., 2005), with of excess $^{210}$Po is diffusion and/or advection from the bottom sediment, especially during low-oxygen summer months.

### 1.3.2 Polonium as a Proxy for POC Flux

The sequestration of atmospheric carbon, otherwise known as the biological pump, fixes between 10 and 20 Gt of carbon dioxide to particulate organic carbon (POC) that sinks out of the euphotic zone each year (Stewart et al., 2007). Assessing the efficiency of this biological pump is necessary in order to determine the ocean's role in controlling anthropogenic $CO_2$. Using a particle-reactive short-lived natural radionuclide, such as $^{210}$Po, can provide a unique insight in the quantification of POC export from the surface ocean to the sediment surface on the ocean floor (Stewart et al., 2007). The grandparent of $^{210}$Po, $^{210}$Pb, is also particle-reactive which can make the determination of POC flux complicated. However, since $^{210}$Po has a higher affinity for organic particles than $^{210}$Pb, it does produce a deficit in the surface eutrophic layers of the water column, and this process can be studied to successfully predict POC export (Stewart et al., 2007).

$^{210}$Po has been utilized as a proxy for particle transfer in the oceanic water column (Radakovitch et al., 1999), ocean circulation (Moore and Smith, 1986), and vertical flux of particulate matter in the ocean (Nozaki et al., 1997, 1998; Friedrich and Rutgers van der Loeff, 2002). Similar to the relationship between $^{238}$U and $^{234}$Th, radioactive $^{210}$Pb and $^{210}$Po should come to secular equilibrium on a rough time scale of 2 years; however the two are rarely in equilibrium in the surface layer of the ocean (Cochran et al., 1983; Nozaki et al., 1997, 1998). This disequilibrium is often due to the

varying particle affinities of lead and polonium. Hong et al. (1999) report that in the upper ocean, the average dissolved $^{210}Po/^{210}Pb$ activity ratio is near 0.5 rather than 1, which would be true if the radioisotope pair were in secular equilibrium. This implies that $^{210}Po$ is preferentially removed from surface waters because of the different affinities that $^{210}Po$ and $^{210}Pb$ have for particulate matter (Stewart and Fisher, 2003a). There is also a strong correlation between the dissolved $^{210}Po$ removal rate constant and chlorophyll *a* concentrations, but no similar correlation exists for $^{210}Pb$, which suggests link between phytoplankton abundance and $^{210}Po$ removal (Nozaki et al., 1998). Therefore, $^{210}Po$ is highly correlated to sinking particulate organic carbon (POC) while $^{210}Pb$ and $^{234}Th$ activities are correlated to both POC and biogenic silica (Stewart et al., 2007).

The short half-life of $^{210}Po$ (approximately 5 months) allows the study of POC flux to be relevant on the seasonal and $^{210}Pb$ – $^{210}Po$ disequilibria in the water column has been successfully utilized in measuring the flux of carbon from the surface ocean (Hong et al., 2013; Verdeny et al., 2008; Stewart et al., 2007).

### 1.4 Importance and Toxicity of Polonium

The primary hazard associated with polonium is its radioactivity, as an alpha emitter. Even in microgram amounts, handling $^{210}Po$ is extremely dangerous. Polonium bioaccumulates in the marine food web and provides its largest doses to aquatic organisms. The concentration of $^{210}Po$ is approximately $\geq$148 mBq $g^{-1}$ in phytoplankton (Cherry, 1964), approximately 3,145 mBq $g^{-1}$ in shrimp hepatopancreas (Cherry and Heyraud, 1981), approximately $\leq$700 and $\leq$1,026 mBq $g^{-1}$ in mussel soft tissue (Germain et al., 1995) and hepatopancreas (Stepnowski and Skwarzec, 2000), respectively, and

approximately ≤262 mBq $g^{-1}$ in fish (Clulow et al., 1998). This data suggests apparent bioaccumulation of polonium in the marine food web. In contrast, humans have an average $^{210}$Po concentration of 0.148 mBq $g^{-1}$, yielding a dose that is about two orders of magnitude lower than those received by marine animals (Cherry, 1964), in normal circumstances.

Higher than normal $^{210}$Po concentrations have also been found in filter feeding species such as the scallop *Chlamys varia*, specifically in the digestive gland (Bustamante et al., 2002). Sub-cellular investigations have shown that approximately 40% of the $^{210}$Po contained in the digestive gland is in the cytosolic fraction and suggests a high bioavailability of the $^{210}$Po in this fraction can move into the higher trophic levels. In fact, estimates demonstrate that approximately 4 kg of scallop flesh intake would be sufficient enough to reach the annual permissible intake of 1 mSv of $^{210}$Po for humans (Bustamante et al., 2002).

## 1.5 Thesis Goals and Objectives

The goal of this thesis is to accurately and effectively address $^{210}$Po dynamics in the northern Gulf of Mexico hypoxia zone and understand POC flux in the Gulf of Mexico. Samples have been collected for $^{210}$Po and $^{210}$Pb activity measurement in the water column for both dissolved and particulate phase from three scientific cruises. Two cruises focus on the shallow Louisiana continental shelf. These two cruises took place during the peak hypoxia months during summer 2011 and summer 2012. The samples from these expeditions will provide insight for $^{210}$Po remobilization mechanisms in coastal hypoxic waters. Another cruise focuses on the open ocean environments of the Gulf of Mexico along a North-South transect starting at the mouth of the Atchafalaya

River, taking place in August 2011. Samples from this cruise have been analyzed to study particulate organic carbon (POC) flux in the open ocean, by studying the $^{210}$Pb – $^{210}$Po disequilibria in the water column.

The overreaching goal of this thesis research is to understand Polonium dynamics in low oxygen coastal environments and to utilize $^{210}$Po as a radiotracer for POC flux in the open ocean. I will take a two-tiered approach to this thesis and address these topics separately in the following chapters. Chapter 2 will address $^{210}$Po remobilization from low oxygen sediments in the seasonally hypoxic zone of the Northern Gulf of Mexico. The seasonal hypoxia zone in the northern Gulf of Mexico makes this area the perfect study site to quantify $^{210}$Po remobilization in a coastal setting. Chapter 3 will review $^{210}$Po based POC fluxes in the Gulf of Mexico. There have been a very limited number of studies in the Gulf of Mexico on export of carbon from the surface layers and there have been virtually no studies that determine POC flux using the $^{210}$Pb – $^{210}$Po disequilibria in the water column (Henson et al., 2012).

# CHAPTER 2: POLONIUM-210 REMOBILIZATION IN THE NORTHERN GULF OF MEXICO HYPOXIA ZONE

## 2.1 Introduction

$^{210}Po$ ($t_{1/2}$ = 138.376 d) is the final radioactive end member in the naturally occurring $^{238}U$ decay chain and decays to stable $^{206}Pb$ via decay of $^{210}Bi$ ($t_{1/2}$ = 5.012 d). $^{210}Po$ is produced from the decay of $^{210}Pb$ ($t_{1/2}$ = 22.2 yr). The primary source of $^{210}Pb$ in the natural environment is the exhalation of $^{222}Rn$ ($t_{1/2}$ = 3.8 d) from continents into the atmosphere. Although $^{210}Po$ is produced from $^{210}Pb$ precipitation from the atmosphere, this is activity is negligible because of the short residence time of $^{210}Pb$-containing aerosols in the atmosphere (Harada et al., 1989). Although, most of the $^{210}Po$ in the aqueous environment is related to in situ decay of $^{210}Pb$ (Kim et al., 2005), however Po production can also occur from the in situ decay of $^{226}Ra$ to $^{210}Pb$ and subsequently to $^{210}Po$.

$^{210}Pb$ and $^{210}Po$ are both particle reactive but have varying particle affinities and binding mechanisms. $^{210}Pb$ becomes quickly absorbed to sedimentary particle surfaces, whereas $^{210}Po$ can be incorporated via biological activity into the cytoplasm and cell wall of some species of phytoplankton (Fisher et al., 1983). The partitioning of $^{210}Po$ in biological material is similar to that of protein and sulfur within the cell (Fisher et al, 1983; Stewart and Fisher, 2003A, 2003B). In the water column, the biogeochemical differences between $^{210}Pb$ and $^{210}Po$ result in $^{210}Po$ being more efficiently removed from surface waters in marine and lacustrine environments than $^{210}Pb$, which is removed via scavenging by sinking particles.

In addition to the evidence for a strong biological component in the geochemistry of $^{210}$Po, several studies have shown the organic geochemistry of sulfur is similar to $^{210}$Po (Harada et al., 1989; Balistrieri et al., 1995; Swarzenski et al., 1999). Polonium is considered a class B, sulfur-seeking metal, and is associated with proteins and sulfur-contained compounds (Stewart et al., 2007). Higher trophic level organisms such as marine copepods indicate a relatively high assimilation efficiency of $^{210}$Po by consumption of zooplankton (Stewart and Fisher, 200S12B). The high assimilation efficiency coupled with a slow Po loss rate make zooplankton effective conduits for the transfer of $^{210}$Po to higher trophic levels and bioaccumulation of the radioisotope in the marine food web, which may potentially contaminate seafood. This enrichment among higher trophic levels in the marine environment is primarily derived from the direct consumption of foods rather than from the intake of seawater (Kim et al., 2005). In fact, $^{210}$Po has been found to concentrate in the hepatopancreas of several marine invertebrates; several studies have shown $^{210}$Po to be associated with protein in this organ (Fisher et al., 1983). Polonium activity in the marine food web has been well documented among various studies. For example the activity of $^{210}$Po in phytoplankton has been reported to be $\geq$148 mBq g$^{-1}$ (Cherry, 1964) and 3,145 mBq g$^{-1}$ in shrimp hepatopancreas Cherry and Heyraud, 1981). Several later studies reported $^{210}$Po activities in higher trophic level organisms and found $\leq$700 and $\leq$1,026 mBq g$^{-1}$ in mussel soft tissue (Germain et al., 1995) and hepatopancreas (Stepnowski and Skwarzec, 2000), respectively, and $\leq$262 mBq g$^{-1}$ in fish (Clulow et al., 1998). Uptake of this radioisotope by marine organisms has been well documented in coastal environments in varying locations around the world (Bustamante et al., 2002). In fact,

estimates demonstrate that approximately 4 kg of scallop flesh intake would be sufficient enough to reach the annual permissible intake of 1 mSv of $^{210}$Po for humans (Bustamante et al., 2002). The bioassimilation properties of $^{210}$Po in marine organisms may be enhanced by any supplementary sources of unsupported $^{210}$Po contributing in the water column.

In a closed system, with no interference from particles, we would expect $^{210}$Po and $^{210}$Pb to be in secular equilibrium throughout the entire water column. In this case the activity of both $^{210}$Po and $^{210}$Pb would be equal in both surface and bottom layers of the water column. In a typical marine system, bioassimilation and particle scavenging at the surface decrease the activity of $^{210}$Po. Therefore, in this scenario, $^{210}$Po activity is deficient in the upper water compared to $^{210}$Pb. In an aquatic system that is effected by remobilization or any other supplementary bottom source of $^{210}$Po, we would expect to observe an enrichment of $^{210}$Po relative to $^{210}$Pb in the lower water column layer, but in the surface water $^{210}$Po still deficient to $^{210}$Pb. Due to the parent-daughter relationship of $^{210}$Po and $^{210}$Pb, any supplementary source of $^{210}$Po is identified by an enrichment of $^{210}$Po relative to $^{210}$Po ($^{210}$Pb/$^{210}$Po<1)

Multiple studies have shown $^{210}$Po remobilization from hypoxic sediments in low oxygen lacustrine environments but, to our knowledge, no data for $^{210}$Po remobilization in marine environments exists (Benoit and Hemond, 1990; Kim et al., 2005; Talbot and Andren, 1984). Talbot and Andren (1984) conducted a study on seasonal variations of $^{210}$Po in an oligotrophic lake in Wisconsin, USA. The study revealed a depletion of $^{210}$Po in the surface waters relative to bottom water suggesting a sedimentary source of Po, consistent with other work in seasonally anoxic lakes or ponds (Benoit and Hemond,

1990; Kim et al., 2005). Low oxygen conditions have also been shown to remobilize other radionuclide pairs from the $^{238}U$ decay series, such as $^{226}Ra/^{210}Pb$ (Balistrieri et al., 1995). These authors showed that diffusion of $^{210}Po$ from bottom sediments was occurring but were unable to identify the exact mechanism of remobilization.

Little is known about $^{210}Po$ remobilization from sediments in coastal hypoxic zones. The goal of this study is to identify $^{210}Po$ remobilization in the hypoxic regions of the northern Gulf of Mexico and gain an understanding of the mechanisms that drive remobilization of this radioisotope.

## 2.2 Study Area

The Mississippi river is one of the world's ten largest rivers, with an average annual discharge into the Gulf of Mexico of 430,000 $ft^3\ s^{-1}$ (Bianchi et al., 2010). In the northern Gulf of Mexico, anthropogenic nitrogen is primarily delivered form agricultural fertilizer via the Mississippi river (Bianchi et al., 2010). This input of excess nutrient results in algal production at the surface water. This combined with strong vertical stratification of incoming stream flow and Gulf waters, causes a restriction of oxygen from the atmosphere to the bottom water layers, resulting in the seasonal Gulf of Mexico hypoxia zone, sometimes referred to as the Gulf of Mexico 'Dead Zone'. The Gulf of Mexico 'Dead Zone' lays adjacent to the Mississippi River on the Louisiana/Texas continental shelf with its average size, over the years 2006-2010, being about 17,000 $km^2$ (www.gulfhypoxia.net). Hypoxia in the Gulf of Mexico is generally defined as a dissolved oxygen concentration of $\leq$2 mg $l^{-1}$ (Bianchi et al., 2010). The northern Gulf of Mexico is an important spawning ground for juvenile marine fishes and other organisms and it represents the United States' most economically viable

oyster harvesting area (http://www.epa.gov/gmpo/about/facts.html). The areal extent of the northern Gulf of Mexico Dead Zone, coupled with the potential importance of hypoxia on Polonium geochemistry makes this area an ideal site to study the remobilization of $^{210}$Po from bottom sediments.

## 2.3 Methodology

### 2.3.1 Sample Stations

Water column samples were collected from various stations on the Mississippi/Louisiana/Texas continental shelf from two oceanographic research cruises during the late summer months of 2011 and 2012. Sample collection took place during August 2011 and July/August 2012 and station locations from both years are shown in Figure 2.1. Six water column profiles were collected on the continental shelf for both years, for a total of 12 profiles. Stations are labeled with a prefix ‘S’ which denotes that it is a sample station, followed by a number (11 or 12) indicating the year of collection (2011 or 2012), and ending with a letter A-F indicating the proximity to the mouth of the Mississippi River, where A is closest to the mouth of the Mississippi River and F is furthest away. The intensity and distribution of the hypoxic zone varies both annually and seasonally and the sampling expeditions were planned to collect samples during the hypoxic period (Turner et al., 2002). The number of samples per station was dependent on the depth of the water column. One water sample was taken approximately every 5-7 meters in the water column, with a sample taken approximately 1 m from the water sediment interface.

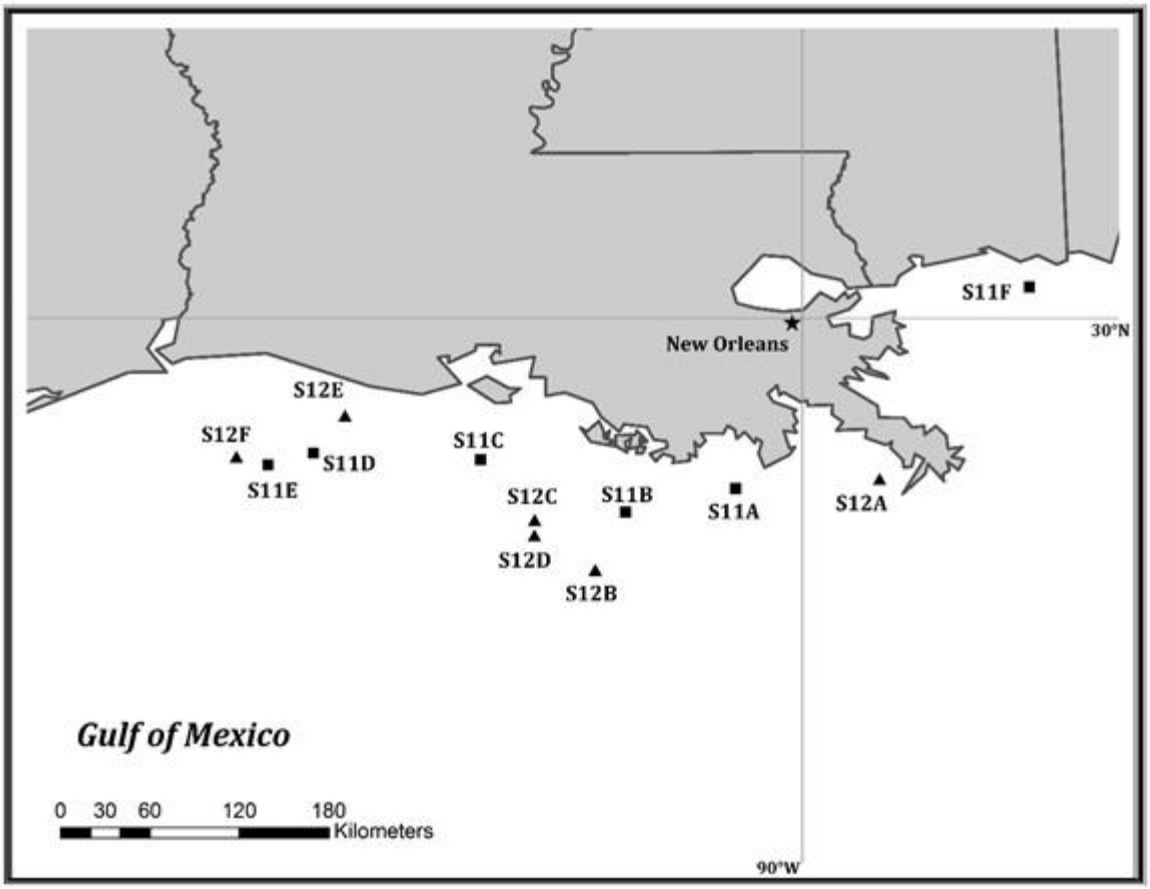

Figure 2.1 The northern Gulf of Mexico and Mississippi River delta. Samples were collected in August 2011 and July/August 2012. Samples collected in 2011 are S11A, S11B, S11C, S11D, S11E, and S11F; Samples collected in 2012 are S12A, S12B, S12C, S12D, S12E, and S12F.

### 2.3.2 Sample Collection

Dissolved water column samples were collected via ship rosette system and consisted of 8-10 liters of seawater. Dissolved oxygen concentrations were recorded with an $O_2$ sensor as part of the ships CTD system. Once collected, samples were immediately filtered on-board using a 0.45 µm nuclepore filter to separate any particulate matter. Water samples were transferred to acid-cleaned polycarbonate containers and acidified with concentrated HCl to pH 1-2. Samples were then spiked with known amounts of $^{209}Po$ and stable $Pb^{2+}$ yield monitors to quantify any subsequent losses of Po and Pb. A $Fe^{3+}$ co-precipitate (30 mg of $FeCl_3$) was also added to each

sample and after an equilibration period of 6-8 hours, the pH was brought back up to approximately pH 8-8.5, using concentrated $NH_4OH$. Samples were allowed to precipitate and settle for 8-10 hours. Then the precipitate was transferred to 1 L polypropylene bottles. One liter bottles were stored on board for processing upon arrival to shore. Further radiochemical purifications and measurements were conducted back in the laboratory at Louisiana State University to determine the final $^{210}Po$ and $^{210}Pb$ activities. The $^{210}Po$ analytical methods used to determine $^{210}Po$ activity in the water column are similar to those described in Nozaki (1986) and Masque et al. (2002).

2.3.3 Analytical Methods

Polonium was auto-deposited directly on to silver planchets following methods described by Flynn (1968) and Fleer & Bacon (1984). After the initial plating of Polonium onto the silver planchets was complete, a 1 mL aliquot was extracted directly from the sample and these aliquots were used to determine the yield of $^{210}Pb$ by measuring the $Pb^{2+}$ via ICP-OES. The plating solutions were then cleaned of all residual Polonium remaining using an AGX-I resin column, re-spiked with $^{209}Po$ yield tracer and stored for 9-10 months, allowing $^{210}Po$ to be regenerated from the decay of $^{210}Pb$. This freshly produced $^{210}Po$ represented the concentration of $^{210}Pb$ in the original sample (Swarzenski, 1999).

The silver planchets used to measure both $^{210}Po$ and $^{210}Pb$ were then counted on Canberra Alpha Analyst high-resolution silicon-surface barrier (PIPS) alpha detectors. All decay and volume corrections for $^{210}Po$ and $^{210}Pb$ quantification were derived following Church et al. (2012) and Baskaran et al. (2012).

## 2.4 Results and Discussion

### 2.4.1 General Water Chemistry

Dissolved $^{210}$Po and $^{210}$Pb activities were measured for sample locations in the northern Gulf of Mexico hypoxic zone during August 2011 and July 2012. Sample stations have varying bottom depths and varying degrees of water column stratification (Fig. 2.2 and 2.3). Stratification of different water column parameters such as temperature, fluorescence, density, salinity and dissolved oxygen were highly variable among the different stations and years. However, hypoxic conditions (dissolved oxygen 0-2 mg $l^{-1}$) were observed in the bottom water layers in the majority of the profiles from both 2011 and 2012. Dates of collection and bottom water oxygen concentrations for all sample sites are shown in Table 2.1.

Table 2.1 Sample collection date, location, and geochemical data for all stations.

| **Station** | **Date of Collection** | **Latitude** | **Longitude** | **Bottom $O_2$ (mg/L)** | **Surface $^{210}$Pb/$^{210}$Po** | **Bottom $^{210}$Pb/$^{210}$Po** |
|---|---|---|---|---|---|---|
| S11A | 8/15/2011 | 28.97056 | -90.40194 | 0.5884 | 0.7496 | 0.6300 |
| S11B | 8/14/2011 | 28.83028 | -91.065 | 0.0680 | 0.6066 | 0.4816 |
| S11C | 8/5/2011 | 29.14694 | -91.94167 | 0.1221 | 1.1896 | 0.5787 |
| S11D | 8/2/2011 | 29.18472 | -92.95056 | 0.8547 | 2.0798 | 1.3199 |
| S11E | 8/4/2011 | 29.115 | -93.22361 | 4.8968 | 1.2569 | 0.9350 |
| S11F | 8/17/2011 | 30.18889 | -88.62917 | 4.1061 | 1.1092 | 0.6102 |
| S12A | 7/22/2012 | 29.03178 | -89.53374 | 2.7041 | 1.1351 | 0.6514 |
| S12B | 7/24/2012 | 28.48196 | -91.24856 | 2.6294 | 2.6378 | 0.6321 |
| S12C | 7/24/2012 | 28.69036 | -91.61684 | 3.0264 | 0.8078 | 0.4601 |
| S12D | 7/24/2012 | 28.78368 | -91.61574 | 2.9274 | 1.2469 | 0.7986 |
| S12E | 7/25/2012 | 29.41306 | -92.76 | 1.1357 | 5.1551 | 1.6854 |
| S12F | 7/26/2012 | 29.1661 | -93.41502 | 0.7913 | 1.2425 | 0.8207 |

Volume of river discharge into the northern Gulf of Mexico differed greatly from 2011 to 2012. The average annual river discharge was approximately for both 2011 and 2012 based on USGS monitoring station data (waterdata.usgs.gov). Discharge for 2011 was approximately 600,000 $ft^3$ $s^{-1}$ and was 300,000 $ft^3$ $s^{-1}$ for 2012. The average annual discharge for the Mississippi River is 430,000 $ft^3$ $s^{-1}$ (Bianchi et al., 2020). Since 2011 was a year of pronounced flooding in the Mississippi River and its tributaries, the Bonnet Carre Spillway was opened to divert the flow of water to Lake Pontchartrain. Nutrient-rich water flowing into Lake Pontchartrain produced hypoxic conditions in the Gulf of Mexico, east of the Mississippi River (Bianchi et al., 2010). One water profile was collected from this area, S11F.

Due to the larger input of fresh water to the northern Gulf of Mexico from the mouth of the Mississippi River during 2011, water column stratification was more defined for this year. Figure 2.2 shows the water column parameters for 2011. This is especially true for stations close to the mouth of the Mississippi River (Fig. 2.2 and 2.3). In most profiles collected in 2011, the bottom 5-6 m exhibited a dissolved oxygen concentrations < 2mg/L. 2012 was a drought year for the Mississippi River and river discharge volume was greatly reduced, approximately half the volumetric discharge measured in 2011 (waterdata.usgs.gov). During 2012, hypoxia but was much less common than in 2011. Figure 2.3 shows that the water column was also less stratified in 2012 than in 2011, which is likely a result of the reduced discharge volume out of the Mississippi River for this year. Additionally, the hypoxic portion of the water column for profiles collected during 2012 was reduced to the bottom 2-3 m in most instances.

Based on the parent-daughter relationship of $^{210}$Po and $^{210}$Pb, in the marine environment we expect to find $^{210}$Po and $^{210}$Pb to be in equilibrium or $^{210}$Po<$^{210}$Pb due to biological uptake by phytoplankton. Understanding this relationship is fundamental when identifying any source of unsupported $^{210}$Po that is being remobilized from low-oxygen sediments. The primary source of $^{210}$Po in the natural environment is the direct decay of $^{210}$Pb. Therefore, the $^{210}$Pb/$^{210}$Po ratio in the bottom layer and surface layer of the water column could reveal valuable information about any potential sources and sinks of unsupported $^{210}$Po.

2.4.2 Dissolved $^{210}$Po in 2011

The water column $^{210}$Po activity during 2011 ranged from a minimum of 1.91±0.1 dpm 100 $l^{-1}$ to a maximum of 10.2±0.52 dpm 100 $l^{-1}$. Similarly, dissolved $^{210}$Pb activities ranged from a minimum of 1.79±0.09 dpm 100 $l^{-1}$ to a maximum of 6.87±0.34 dpm 100 $l^{-1}$. Dissolved $^{210}$Pb concentrations included in our data sets are in the same range as dissolved $^{210}$Pb concentrations in the water column at sample collections sites of similar bottom depths in a study on $^{210}$Pb in the Gulf of Mexico by Baskaran and Santschi in 2002.

Water column profiles are arranged in order of proximity from the mouth of the Mississippi River, as shown in Figure 2.4. S11A and S11B are the closest to the mouth of the river and are the only profiles that have an excess of $^{210}$Po in the surface water. The excess of $^{210}$Po with respect to $^{210}$Pb in surface water for these profiles is likely due to remnants of organic particulate matter that are being discharged from the river. Fluorescence and beam attenuation data, Figure 2.2, for these sites in 2011 suggest more particulate matter in the upper water column than in 2012, Fig. 2.3.

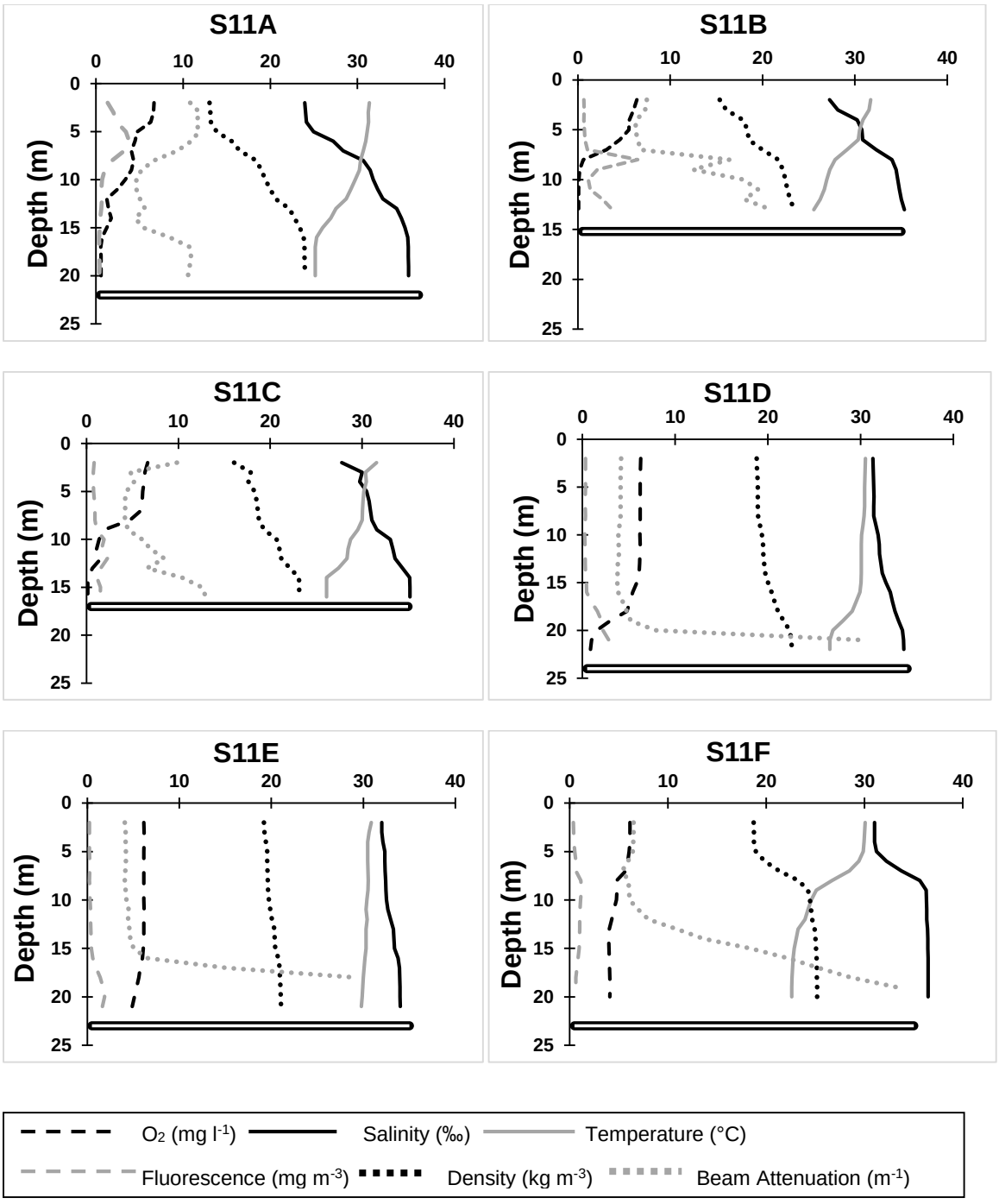


Figure 2.2 Water column parameters for stations in 2011. Includes $O_2$, Temperature, Salinity, Density, Beam Attenuation, and Fluorescence. Horizontal line denotes sediment surface.

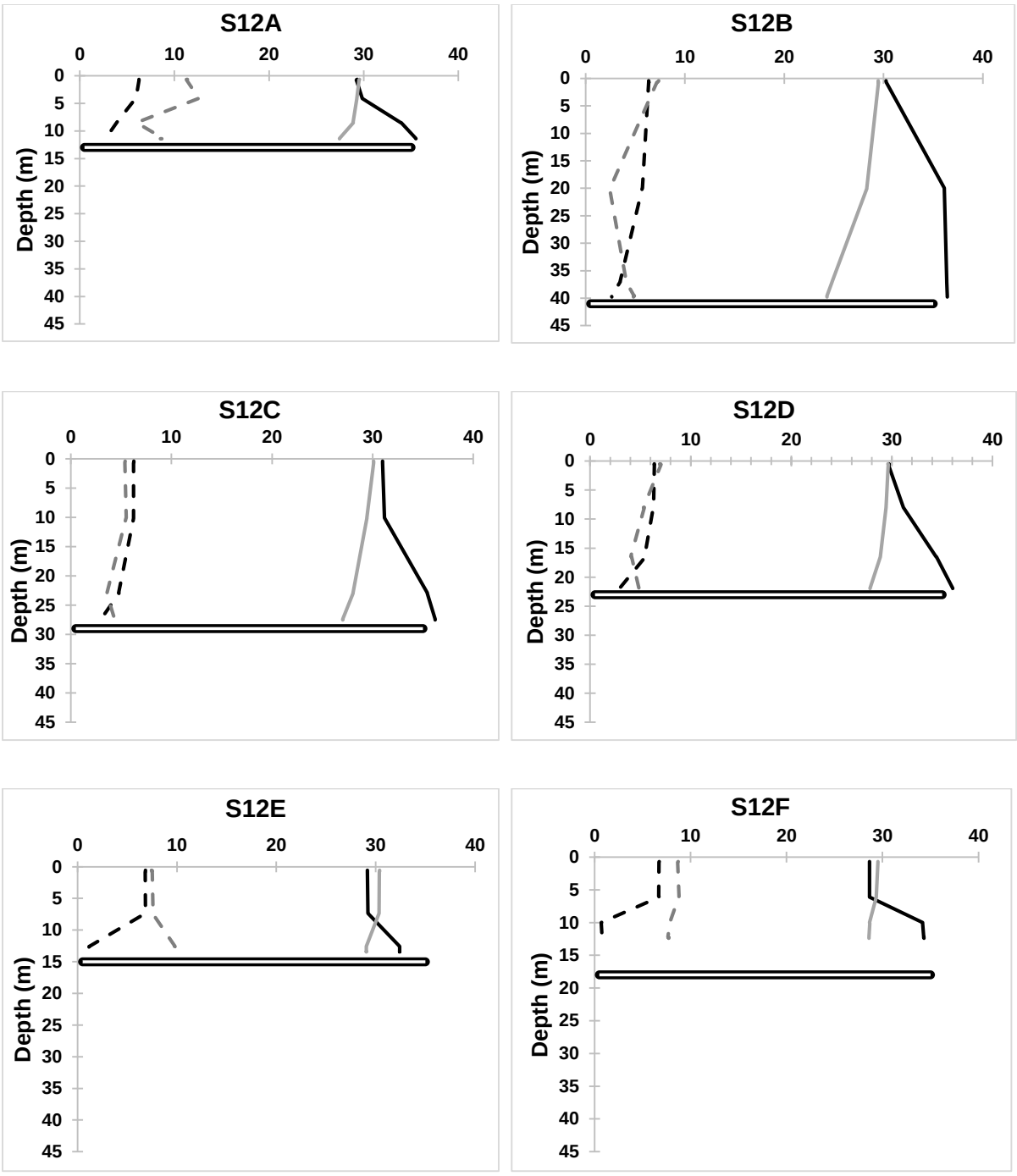


Figure 2.3 Water column parameters for stations in 2012. Includes $O_2$, Salinity, Fluorescence, and, Temperature. Horizontal line denotes sediment surface.

$^{210}$Po surface concentration at sample station S11A was 3.94±0.2 dpm 100l$^{-1}$ and at S11B this concentration was slightly higher at 4.76±0.24 dpm 100l$^{-1}$. The excess $^{210}$Po in the upper water column for these two sites is likely a product of the degradation of organic material introduced by the Mississippi River. S11A and S11B are the only stations tested in both 2011 and 2012 that show an excess of $^{210}$Po in surface water and are also the most proximal to the mouth of the river. Fluorescence data from these profiles show about twice the amount of organic content in the 5-10 m depth compared to the other profiles from 2011. Fluorescence values for S11A and S11B in the 5-10 m depth range are 2.33 and 2.03 mg m$^{-3}$ respectively while the stations further from the discharge zone are well below 1 mg m$^{-3}$. An increase in $^{210}$Po in surface water due to input of organic matter from rivers has also been seen in similar deltaic systems in Malaysia (Theng et al., 2005).

The surface $^{210}$Po concentration in sample station S11C is lower than the $^{210}$Pb concentration. The enrichment of $^{210}$Pb relative to $^{210}$Po in the surface water is expected based on the parent-granddaughter relationship of $^{210}$Po and $^{210}$Pb, especially as stations move west away from the mouth of the Mississippi River. Surface $^{210}$Po concentration at S11C is 3.47±0.17 dpm 100l$^{-1}$ and surface $^{210}$Pb concentration is 4.13±0.21 dpm 100l$^{-1}$. S11D also shows an enrichment of $^{210}$Pb relative to $^{210}$Po in the surface waters. Station S11D is further from the source of biological material, the Mississippi River. S11E also shows enrichment of $^{210}$Pb in the surface water relative to $^{210}$Po and is the most westerly sample collection station in 2011. Surface $^{210}$Po concentration in stations S11D and S11E are 2.32±0.11 dpm 100l$^{-1}$ and 3.23±0.16 dpm 100$^{-l}$, respectively.

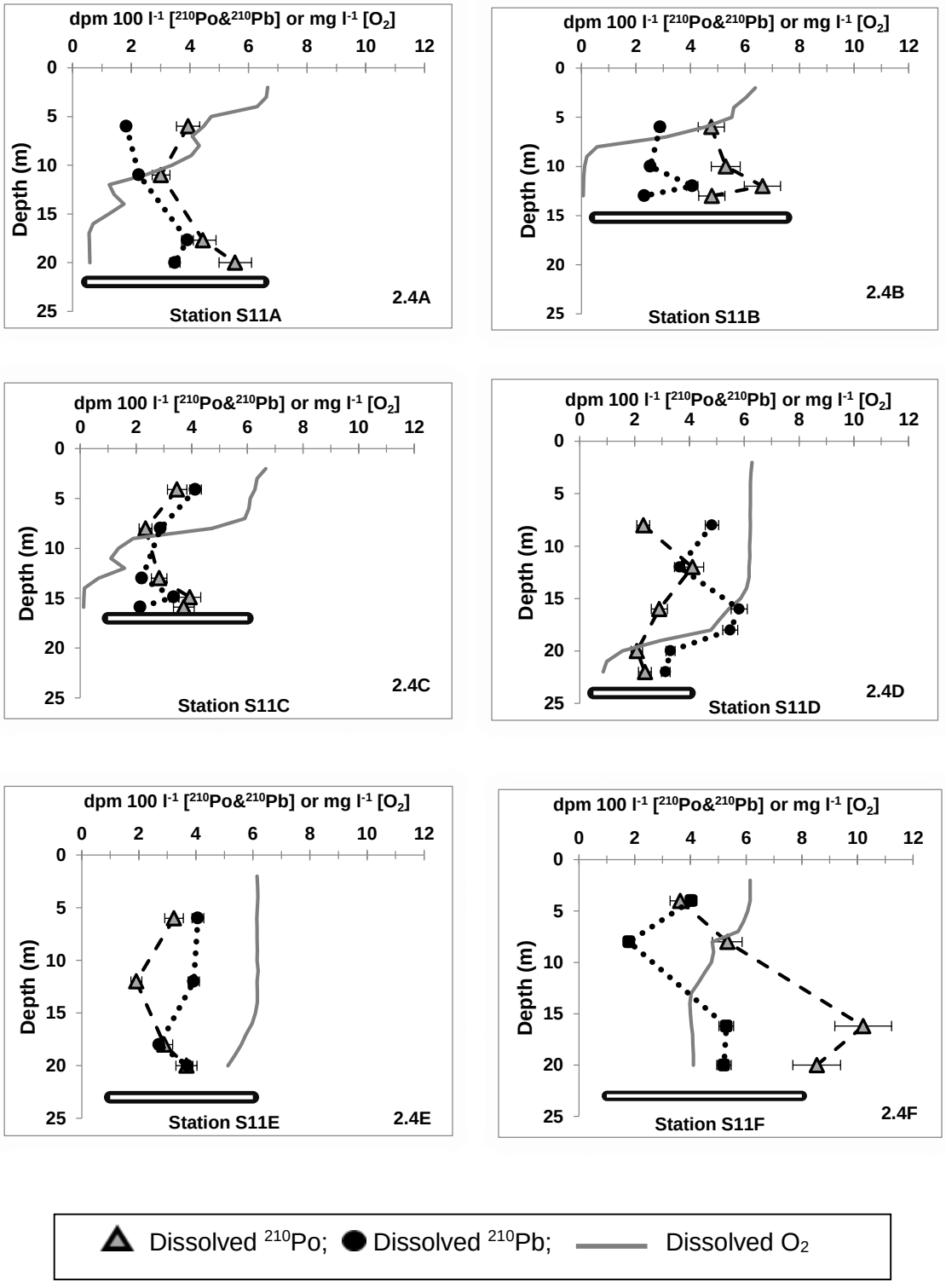


Figure 2.4 Dissolved $^{210}$Po and $^{210}$Pb activity in the water column from sample stations in the northern Gulf of Mexico from 2011. Horizontal Line denotes bottom depth.

Sample station S11F is the only station located east of the Mississippi River mouth. However, as previously mentioned, 2011 was considered a year of high annual discharge for the Mississippi River and due to this excess discharge, water was diverted to Lake Pontchartrain to ease flooding in New Orleans, LA. Based on water column dissolved oxygen data for this area, the excess volume of river water introduced may have created a localized hypoxia east of the Mississippi River, off the coast of Gulf Port, Mississippi. Water column profile S11F is from this region. $^{210}$Po concentration is nearly in equilibrium with $^{210}$Pb concentration in the surface water.

The $^{210}$Po concentration for bottom water in all water column profiles collected in 2011 show an increase relative to the concentration in surface water. Table 2.1 shows the surface and bottom $^{210}$Pb/$^{210}$Po ratios for all sample stations in 2011 and 2012. Bottom $^{210}$Po concentration in the lower water column layers increased at site S11A relative to the surface concentration of $^{210}$Po. Despite the excess $^{210}$Po in the surface water for this site, the two radioisotopes are in equilibrium throughout most of the water column (Fig. 2.4A). Therefore, $^{210}$Po activity on the surface does not affect $^{210}$Po in the bottom water layers. The surface $^{210}$Pb/$^{210}$Po ratio was 0.75 in the surface water for this site and decreased to 0.63 in the samples collected near the bottom. More $^{210}$Po is present near the bottom water layers, which are also characterized by a decrease in $^{210}$Pb. This suggests a supplementary source of $^{210}$Po to the lower water column. Station S11B is geochemically and geographically similar to S11A. Both are proximal to the mouth of the river and $^{210}$Po is enriched relative to $^{210}$Pb throughout the water column. Despite this enrichment via riverine influence, we see a decrease in the $^{210}$Pb/$^{210}$Po ratio from the surface to bottom water layers. In the surface, this ratio is 0.61

and this value decreases to 0.48 in the bottom water, which is indicative of unsupported $^{210}$Po near the bottom water. This region closest to the mouth of the river is where we found the most defined stratification in the water column (Fig. 2.1)

The $^{210}$Pb/$^{210}$Po ratio in particulate matter of samples collected at stations S11A and S11B is below1. This is an example of the way particles can preferentially be taken up by Po over Pb in the water column. A study on $^{210}$Po and $^{210}$Pb activities in water column profiles at a river mouth in Malaysia show $^{210}$Po enrichment relative to $^{210}$Pb. The $^{210}$Pb/$^{210}$Po ratios were well above 1 for some sites and in one case above 28, indicating an excess of unsupported $^{210}$Po in the water column and possible supplementary source (Theng and Mohamed, 2005).

The $^{210}$Pb/$^{210}$Po ratio of dissolved concentrations for S11C is over 1.19 near the surface water and near the bottom water is 0.57, which reveals a relative enrichment of Po with respect to Pb in the bottom water layers. $^{210}$Pb and $^{210}$Po concentrations mirror each other throughout the water column but immediately below the stratified layer at approximately the 9 m depth, $^{210}$Po concentration surpasses $^{210}$Pb.

The $^{210}$Pb/$^{210}$Po ratio for station S11D ranged from 2.08 near the water column surface, decreasing to 1.31 near the bottom. Although this profile did show a $^{210}$Pb/$^{210}$Po less than 1 in the bottom water column layer, it does exhibit a relative increase in $^{210}$Po, with a corresponding decrease in $^{210}$Pb. Below the 20 m water depth, $^{210}$Po is increasing from 2.08±0.1 dpm 100 $l^{-1}$ to 2.37±0.12 dpm 100 $l^{-1}$. Considering the parent daughter relationship of these two radioisotopes, we would expect to observe a decrease in $^{210}$Po concentration that matches the decrease in $^{210}$Pb concentration. This, along with a drop in the $^{210}$Pb/$^{210}$Po ratio in the bottom water layers, may suggest a supplementary bottom

source of $^{210}$Po, as the bottom water dissolved oxygen concentration decreases below 2 mg $l^{-1}$.

Sample station S11E is unique in that the dissolved oxygen concentration never reaches hypoxic conditions or exhibits a well stratified water column, however it does show characteristics of $^{210}$Po remobilization in the lower water column. The general profile of S11E shows $^{210}$Po deficient relative to $^{210}$Pb throughout most of the water column but near the bottom layers the two members of the parent-daughter come close to equilibrium with a concentration of approximately 3.69±0.18 dpm 100 $l^{-1}$. This substantial increase in $^{210}$Po concentration with respect to $^{210}$Pb suggests a bottom supplementary source. Based on the observation that $^{210}$Po remobilization is occurring in waters that are not fully hypoxic suggests that remobilization and hypoxia are happening on different time scales. Due to physical processes like wind, waves, tides, etc., a marine environment, such as the Gulf of Mexico, undergoes a much higher degree of mixing throughout the water column versus an enclosed body of water such as a lake. It stands to reason that there is another chemical or physical process that is driving the remobilization of $^{210}$Po.

In the surface water at S11F, $^{210}$Po and $^{210}$Pb are in equilibrium. $^{210}$Po concentration is 3.62±0.18 dpm 100 $l^{-1}$ and $^{210}$Pb is 4.02±0.2 dpm 100 $l^{-1}$. However, near the bottom of the water column $^{210}$Po concentration increases well beyond $^{210}$Pb concentration. Near the bottom sediment, dissolved $^{210}$Po concentration is 8.53±0.42 dpm 100 $l^{-1}$, while $^{210}$Pb concentration is 5.21±0.26 dpm 100 $l^{-1}$. Also, at the 16 m depth, near the bottom of the water column, $^{210}$Po concentration reaches a high of 10.2±0.51 dpm 100 $l^{-1}$. $^{210}$Pb/$^{210}$Po changes from 1.11 at the surface to 0.61 near the bottom

sediment. Salinity values from this near-shore station shows that it is likely being affected by the output of fresh water from Lake Pontchartrain.

From the 2011 data, dissolved oxygen stratification and concentration near the bottom water (Fig. 2.2 and 2.33), are highly variable. Hypoxic conditions (dissolved oxygen concentration of 0-2 mg/L) are observed in all profiles except S11E and S11F. Marine systems, especially close to the shore, are constantly undergoing mixing throughout the entire water column via waves, wind, and tides. This mixing may oxygenate waters that were previously hypoxic, which is potentially shown in profiles S11E and S11F. If this is true, this suggests that though $^{210}$Po remobilization is driven by low oxygen conditions, $^{210}$Po remobilization occurs on a different time scale once hypoxic parameters are established. This is significant because this discounts dissolved oxygen concentration as an effective indicator of $^{210}$Po remobilization.

### 2.4.3 Dissolved $^{210}$Po in 2012

Samples collected in 2012 were taken from similar, but not the exact locations as stations in 2011. All samples in 2012 were collected from the Louisiana continental shelf, west of the mouth of the Mississippi River. 2011 was a year of high river discharge, as flooding was prevalent. In 2012, however, the northern Gulf of Mexico saw much less fresh water input than in 2011, and 2012 was considered a drought year. This change in fresh water and excess nutrient input in the marine ecosystem potentially affected the stratification and degree of hypoxia in our stations. Profiles collected in 2012 show a more mixed water column than in 2011 (Fig. 2.3). Thus, not all of the sample stations in 2012 exhibit a bottom oxygen concentration less than 2 mg $l^{-1}$. However, there is a sufficient amount of water column stratification to show

remobilization $^{210}$Po from bottom sediments. $^{210}$Po concentration ranged from 0.88±0.04 dpm 100l$^{-1}$ to 4.66±0.23 dpm 100l$^{-1}$ and $^{210}$Pb concentration ranged from 1.13±0.057 dpm 100l$^{-1}$ to 8.67±0.43 dpm 100l$^{-1}$ for the 2012 sample collection year.

Samples collected in 2012 are arranged by proximity to the mouth of the Mississippi River. Due to a larger volume of water discharged from the Mississippi River in 2011 compared to 2012, there was likely more particulate and biological material to be present at the stations closest to the mouth of the river. This is shown by elevated beam attenuation and fluorescence values in the upper water column for S11A in Figure 2.2. The excess biological material produced by the riverine discharge may have created an excess of $^{210}$Po concentration throughout the water column. Since river discharge was much lower in 2012, we did not see this excess in $^{210}$Po concentration in stations near the mouth of the river. All water column profiles collected show a relative deficiency of $^{210}$Po with respect to $^{210}$Pb in the surface water and a subsequent increase of $^{210}$Po with respect to $^{210}$Pb in the bottom water layers, which is suggestive of a supplementary source of $^{210}$Po via remobilization.

The water column profile collected at S12A is the closest to the mouth and of the Mississippi River and directly adjacent to the Mississippi River delta. Salinity values (Fig. 2.3) for this water column shows weak stratification based on salinity and dissolved oxygen in the water column. Fresh water (salinity=29.3-29.8 ‰) resides in the upper 4 m of the water column and salty, more dense water sits at the bottom of the water column. From 4-11 m, salinity ranges from 29.9-35.5 ‰. Dissolved oxygen concentration in the upper water column is characteristic of near the source or mouth of the river. The dissolved oxygen concentration is greater than 6 mg l$^{-1}$ in the upper water

layers but decreases to 2.71 mg $l^{-1}$ in the bottom layers of the water column (Table 2.1). In the upper water column, $^{210}$Po activity is slightly lower than $^{210}$Pb activity. In this top layer, $^{210}$Po concentration is 2.84±0.14 dpm 100$l^{-1}$ and $^{210}$Pb concentration is slightly higher at 3.23±0.16 dpm 100$l^{-1}$. In the bottom water, however, $^{210}$Po concentration increases to 4.66±0.23 dpm 100$l^{-1}$. Subsequently, $^{210}$Pb concentration slightly decreases to 3.04±0.15 dpm 100$l^{-1}$. At this station the $^{210}$Pb/$^{210}$Po ratio is suggestive of $^{210}$Po remobilization in the bottom water, near the sediment. This ratio is 1.35 in the surface water and 0.65 in the bottom water. Shown in Figure 2.5, $^{210}$Po concentration remains constant throughout the water column and rapidly increases around the 8 m depth. This rapid increase in the concentration of $^{210}$Po near the lower water column is suggestive of $^{210}$Po remobilization from low oxygen sediments.

Sample station S12B is the deepest water column profile collected for both 2011 and 2012. The maximum depth was 40 m and though there is minimal effect of river discharge in this area, the sample station exhibited well defined stratification in the water column. The top 19 m of the water column had a salinity of approximately 30 ‰, while the rest of the water column was composed of much more dense water with a 36 ‰. Dissolved oxygen was also well stratified, although conditions did not go below 2 mg $l^{-1}$. The bottom dissolved oxygen concentration was 2.63 mg $l^{-1}$ at this sample station. In the surface water, $^{210}$Pb concentration is more than double the $^{210}$Po concentration. This $^{210}$Po deficiency in the surface water is expected due to polonium's affinity for biological particles. At approximately the 15 m depth in the S12B water column $^{210}$Po concentration exceeds $^{210}$Pb concentration and $^{210}$Po remains in excess of $^{210}$Pb through the extent of the profile.

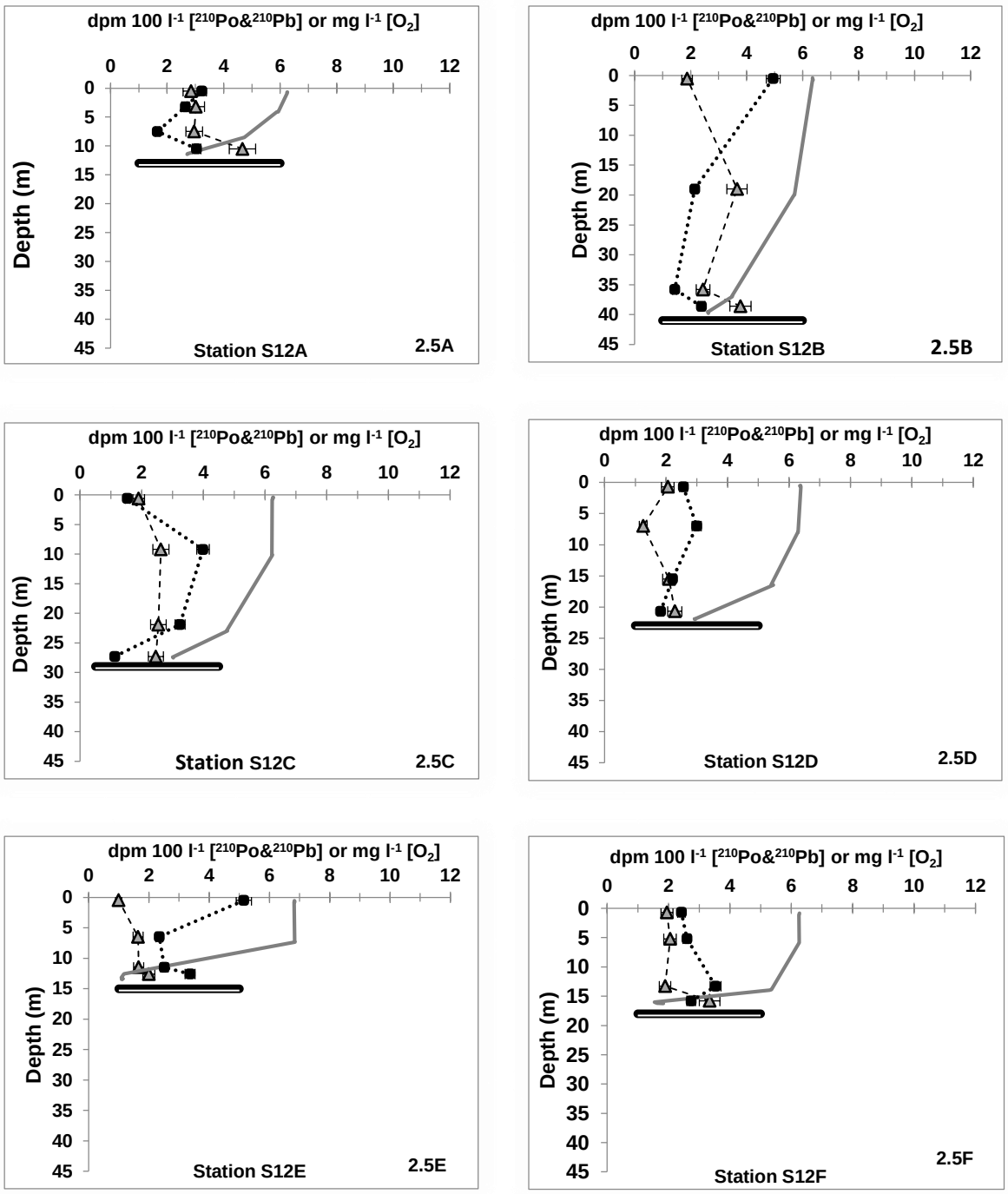


Figure 2.5 Dissolved $^{210}$Po and $^{210}$Pb activity in the water column from sample stations in the northern Gulf of Mexico from 2012. Bottom depth denoted by horizontal line.

The profiles of $^{210}$Po and $^{210}$Pb below 5 m are similar in shape but $^{210}$Po concentration is about double the concentration of $^{210}$Pb. This substantial increase in $^{210}$Po concentration in the intermediate and lower water column is suggestive of a supplementary source of $^{210}$Po. In the surface water, $^{210}$Po concentration is 1.88±0.094 dpm 100l$^{-1}$ and $^{210}$Pb concentration is 4.95±0.25 dpm 100l$^{-1}$ and in the bottom water layer, $^{210}$Po concentration is 3.78±0.19 dpm 100l$^{-1}$ and $^{210}$Pb concentration is 2.38±.012 dpm 100l$^{-1}$. The $^{210}$Pb/$^{210}$Po ratio, shown in Table 2.1 change drastically from 2.63 on the surface to 0.63 in the bottom water. A bottom source of $^{210}$Po in the water column is evident in the S12B sample station. Considering the primary source of $^{210}$Po in the natural environment, this enrichment is only possible if there is a source of unsupported $^{210}$Po.

Sample station S12C is also a relatively deep station and lies west of the mouth of the Mississippi River. This station exhibited weak stratification and the bottom dissolved oxygen concentration was recorded at 3.02 mg l$^{-1}$. In the surface waters, $^{210}$Po and $^{210}$Pb are in equilibrium, and at 10 m depth, $^{210}$Pb concentration is approximately twice the concentration of $^{210}$Po. The remobilization of $^{210}$Po is evident in bottom water here as $^{210}$Pb decreases near the water-sediment interface while $^{210}$Po concentration remains constant. The surface $^{210}$Pb/$^{210}$Po is 0.81 and the bottom ratio is 0.46. Even though the $^{210}$Po concentration remains fairly constant throughout the water column, changes in $^{210}$Po imply a near-bottom Po supply.

Sample station S12D was collected very close to S12C. Therefore the dissolved oxygen and salinity profiles are very similar. The bottom dissolved oxygen concentration is 2.92 mg l$^{-1}$. The surface $^{210}$Po concentration is 2.05 dpm 100$^{-1}$ and the $^{210}$Pb

concentration is 2.56 dpm $100l^{-1}$. Throughout the profile, $^{210}Po$ is deficient relative to $^{210}Pb$ until the deepest 6 m the two radioisotopes achieve equilibrium at the 15 m depth and then $^{210}Po$ concentration is slightly increases greater than $^{210}Pb$ concentration. This slight increase is within error so it is difficult to determine if $^{210}Po$ activity is greater than $^{210}Pb$ activity or the two are in equilibrium. The $^{210}Pb/^{210}Po$ at the surface versus the bottom layer suggests that there is a bottom source of $^{210}Po$ supplying unsupported material to the water column. The surface ratio is 1.25, while the bottom is 0.79.

Station S12E is further west along the Louisiana/Texas continental shelf and shows a substantial increase in the $^{210}Pb/^{210}Po$ ratio from surface water to bottom water layers; ranging from 5.15 to 1.68. This ratio shows much more $^{210}Pb$ than $^{210}Po$ in the upper water column and the two radioisotopes approach equilibrium in the bottom water column layers. This station exhibits a well stratified water but the $^{210}Po$ concentration is not greater than $^{210}Pb$. This suggests there is no simple explanation for the remobilization of $^{210}Po$.

The final sample station collected in 2012, S12F, was the furthest from the mouth of the Mississippi River but still considered a part of the northern Gulf of Mexico hypoxic zone. Throughout the majority of this water column, $^{210}Po$ is deficient relative to $^{210}Pb$. Only close to the sediment-water interface does $^{210}Po$ concentration exceed $^{210}Pb$ concentration. The $^{210}Pb/^{210}Po$ ratio at the surface is 1.27 whereas this ratio near the bottom water is 0.82. This station also showed the lowest dissolved oxygen concentration in the bottom water, 0.79 mg $l^{-1}$. The enrichment of $^{210}Po$ near these low oxygen sediments is indicative of a bottom source of this unsupported radioisotope to the water column.

## 2.5 Discussion

Due to the association of low-oxygen conditions and $^{210}$Po remobilization in anoxic lakes, it was initially assumed that low oxygen would be the driving mechanism of $^{210}$Po remobilization in a coastal environment. However, the relationship between $^{210}$Po remobilization and low dissolved oxygen in the water column is not straightforward and rather complicated. Figure 2.6 shows that there is not a strong correlation between low oxygen and $^{210}$Po activity from stations in 2011 and 2012. This suggest that's $^{210}$Po remobilization and hypoxia are occurring on different time scales within the water column. In a coastal environment, there are currents and tidal forces which mix the water column and the entire water column could be well-oxygenated but still have hypoxic sediments directly below releasing redox sensitive metals. The release of $^{210}$Po

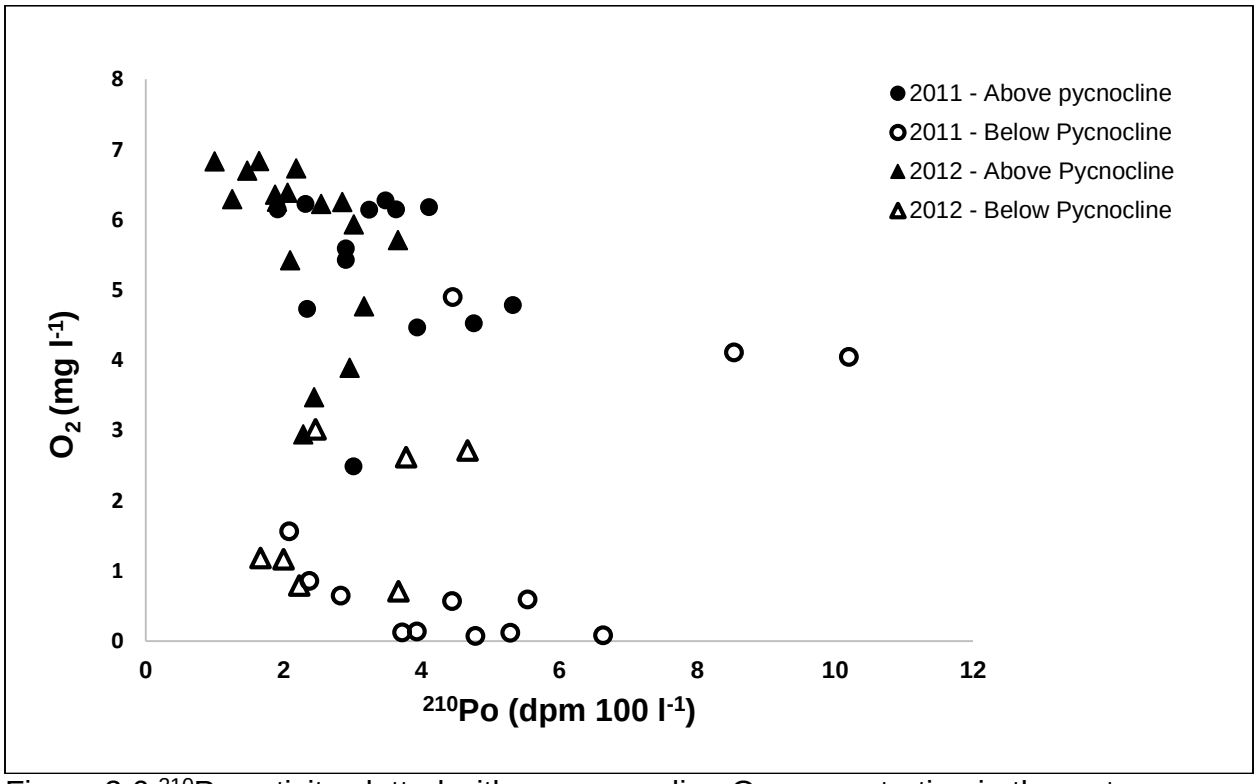


Figure 2.6 $^{210}$Po activity plotted with corresponding $O_2$ concentration in the water column. There seems to be no apparent relationship between dissolved oxygen concentration and $^{210}$Po activity.

from low-oxygen sediments has been linked to the redox cycling of Fe and Mn in some anoxic lake environments. $^{210}$Po and $^{210}$Pb are associated with some transition metals whose rate of solubilization increases with anoxia. $^{210}$Po and $^{210}$Pb have been shown to have similar redox sensitivities to Manganese and Iron, respectively, which may be effective mechanisms driving $^{210}$Po remobilization (Benoit and Hemond, 1990). Additionally, Po has a strong affinity for and bonds directly to Fe. In a study of redox conditions in a seasonally anoxic lake environment, Benoit and Hemond (1990) found $^{210}$Po cycling parallels that of Mn and $^{210}$Pb cycling closely linked to Fe. The diffusion of these redox sensitive elements (Fe and Mn) from the bottom sediments of low oxygen environments can be used as an indicator of $^{210}$Po remobilization (Kim et al., 2005). Additionally, $^{210}$Po has been observed to diffuse from sediments even in the presence of oxygen (Benoit and Hemond, 1990).

Another study done by Swarzenski et al. in 1999 analyzed the dissolved and particulate $^{210}$Po activity in a permanently anoxic fjord in Framvaren, Norway. Dissolved $^{210}$Po activities were highly enriched at the $O_2$/$H_2S$ interface, suggesting redox conditions affect the activity of these radioisotopes in the water column and top sediment layers. In the fjord, the $^{210}$Po/$^{210}$Pb ratio was consistently less than 1.0 in waters above the $O_2$/$H_2S$ boundary while below this boundary, this value increased greater than 4.0 (Swarzenski et al., 1999). This increase is highly reflective of the disequilibria of $^{210}$Po and $^{210}$Pb we observe in the low-oxygen zone of the northern Gulf of Mexico. Among surface waters, dissolved $^{210}$Po is quickly taken up by organic constituents and inorganic Fe/Mn oxides. In the water column and sediment, $^{210}$Po can

be remobilized via biological degradation and redox geochemistry in the northern Gulf of Mexico.

Figure 2.7 shows the $^{210}$Po concentration and total Fe and Mn concentration in the water column from five stations in 2011. In 2.7B and 2.7C (station S11B and S11C, respectively), Mn is being released from the sediment preferentially relative to Fe, which is expected due to the lower redox sensitivities of Mn compared to Fe. $^{210}$Po seems to correlate well with Mn in both 2.7B and 2.7C. In the remaining three profiles, however, this correlation is not apparent. In 2.7A, total Fe and Mn are very low and in 2.7D and 2.7E, we see Fe being released in much greater quantities than Mn. Figure 2.8 shows dissolved Fe and Mn concentration in select profiles from 2011. The dissolved concentration of Fe and Mn in the water column is very similar to the total Fe and Mn concentration (Fig. 2.7) for S11B and S11C. Therefore, these two stations have little interference with particle resuspension or diffusion followed by precipitation. This suggests that the cycling of redox sensitive metals such as Mn and Fe can be used as an effective indicator of $^{210}$Po remobilization in the northern Gulf of Mexico.

Though there is no data from this study to support this idea, the known association of $^{210}$Po with organic matter raises the possibility that polonium is released by the degradation of organic matter in the sediment. Therefore the most likely scenario is that a combination of redox cycling and the degradation of organic matter is the driving mechanism for remobilization of $^{210}$Po in the northern Gulf of Mexico. There must be future research to better understand the redox cycling of transition metals and the degradation of biological material in the northern Gulf of Mexico and how these processes contribute to the remobilization of $^{210}$Po.

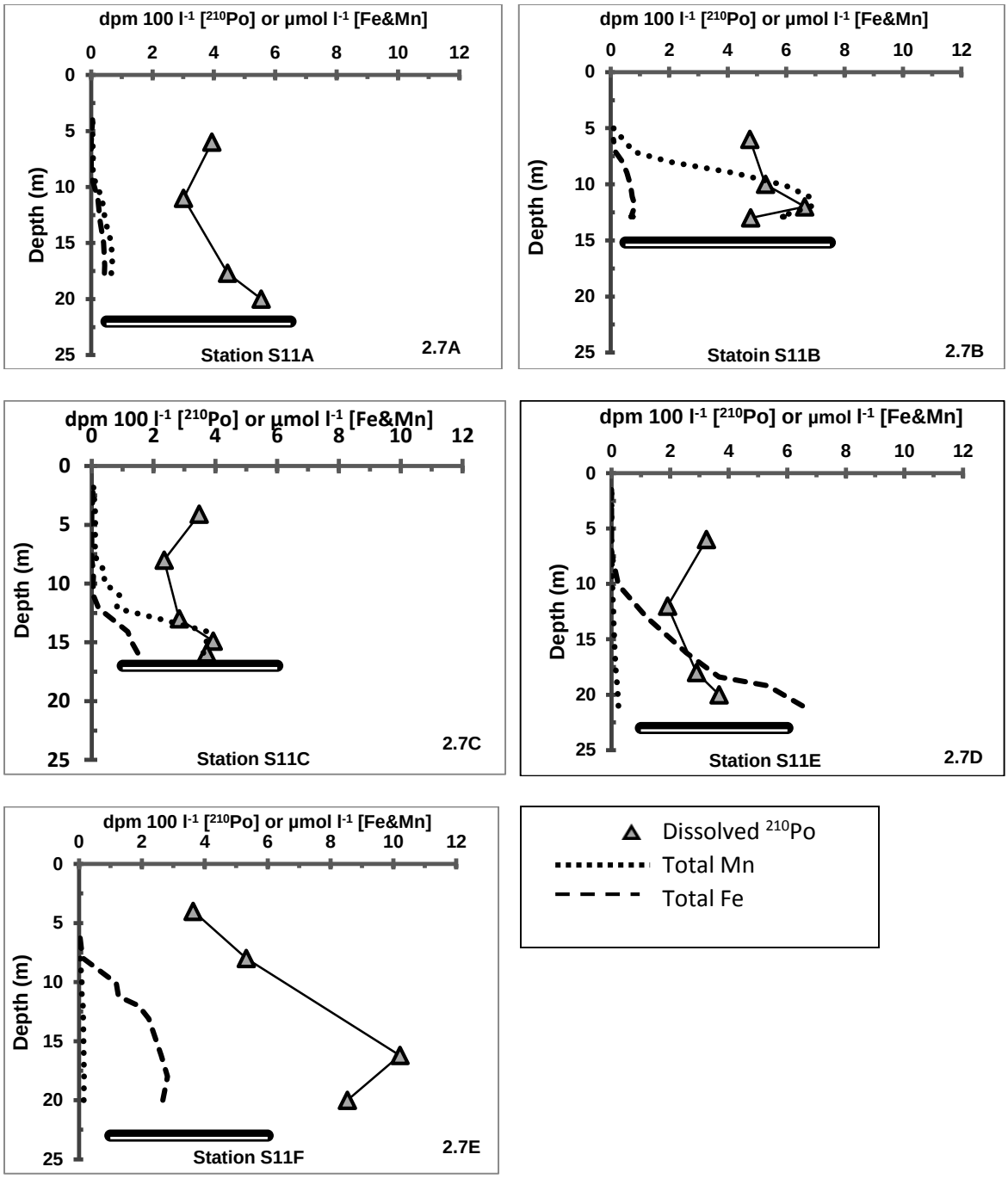


Figure 2.7 Dissolved $^{210}$Po and total Fe and Mn concentration in the water column from select profiles collected in 2011. Data was not available for all profiles. Bottom depth denoted by horizontal line.

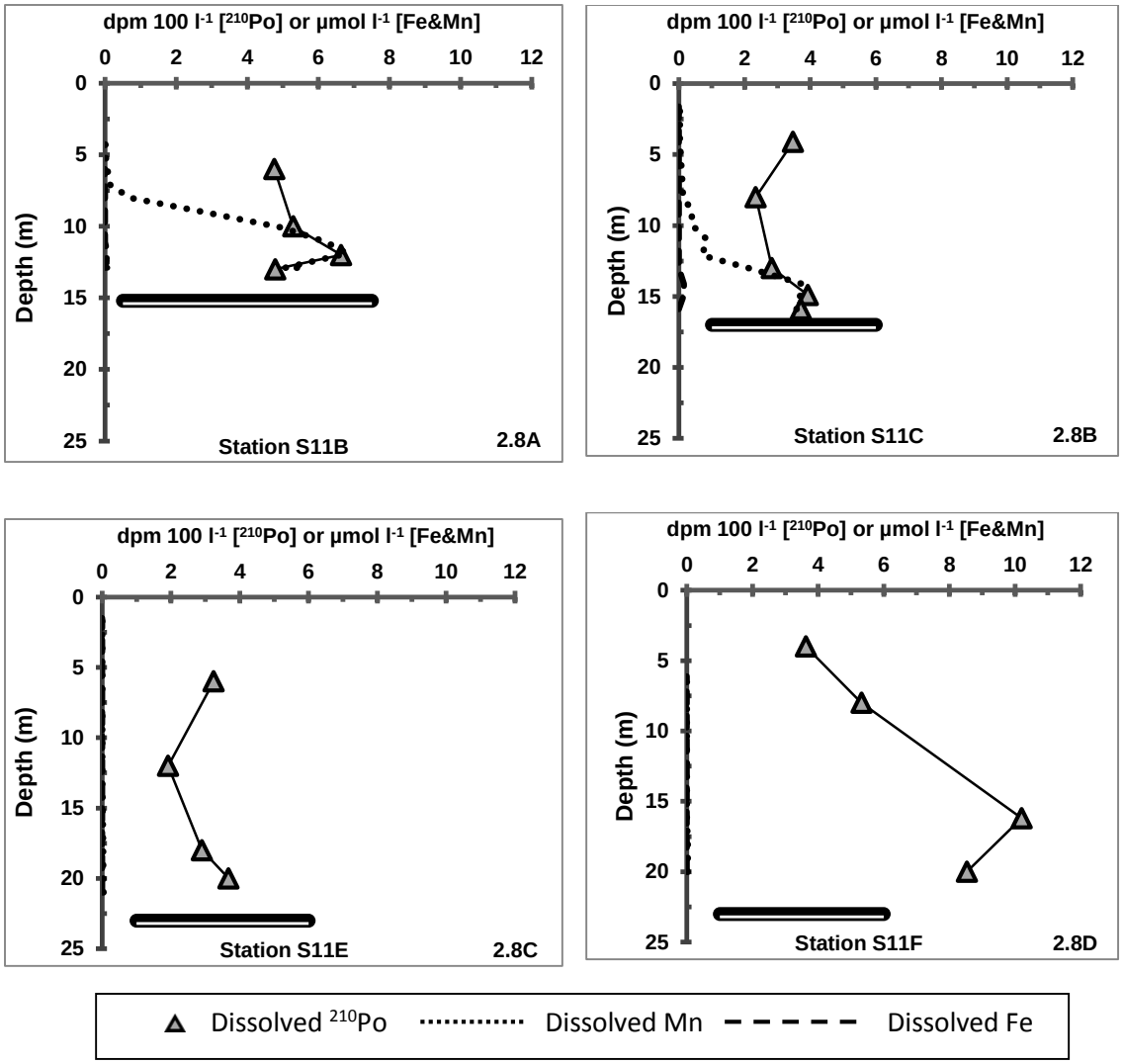


Figure 2.8 Dissolved $^{210}$Po and dissolved Fe and Mn concentration in the water column for select profiles collected in 2011. Data was not available for all profiles. Bottom depth denoted by horizontal line.

## 2.6 Conclusion

This unique study is the first to observe $^{210}$Po remobilization from hypoxic sediments in a coastal marine environment. The seasonal hypoxia that the northern Gulf of Mexico experiences annually makes this area perfect for the study of redox sensitive metal remobilization. We have observed $^{210}$Po remobilization from low-oxygen sediments in 2011 and 2012 based on the $^{210}$Pb/$^{210}$Po ratio in the water column. This

ratio, due to the parent-granddaughter relationship between $^{210}$Po and $^{210}$Pb, suggests the existence of unsupported $^{210}$Po being released from the sediment.

We found no strong correlation between oxygen concentration and $^{210}$Po activity. This is likely due to the dynamic nature of coastal systems which causes hypoxia and remobilization to occur on different time scales. Fe and Mn, two redox sensitive metals with known associations to Po, may be the driving mechanisms for $^{210}$Po remobilization. We saw a correlation between Fe and Mn and $^{210}$Po from select stations in 2011 from this study, unfortunately data for 2012 was not available.

Therefore, future research must investigate the redox cycling of Fe and Mn more closely in the Gulf of Mexico as a function of the rate of the rate of $^{210}$Po remobilization. The flux of $^{210}$Po, Fe and Mn, as well as organic matter from sediments must be determined in order to understand the temporal relationship of these elements. In order to understand the ratio of $^{210}$Po remobilization between Fe/Mn cycling and organic matter degradation, a benthic chamber system would be an ideal instrument to study this change over time. The mechanisms driving the remobilization of $^{210}$Po in the coastal marine environment however is likely a combination of the redox cycling of Fe and Mn and the degradation of organic matter.

# CHAPTER 3: POLONIUM-210 AS A TRACER OF SEASONAL POC EXPORT IN THE GULF OF MEXICO

## 3.1 Introduction

In the upper ocean euphotic zone autotrophs utilize $CO_2$ from the atmosphere to form organic matter. A fraction of this carbon is transported through the water column, as Particulate Organic Carbon (POC). Some POC is remineralized in the upper ocean via microbial activity and the rest is exported to the deep ocean and seafloor. POC is the main source of nutrient for benthic organisms (Honjo et al., 2008; Rocha and Passow, 2007). This sequestration of carbon from the atmosphere and transport to the deep ocean is referred to as the global biological pump. The global biological pump transfers large amounts of atmospheric carbon from the upper ocean, where primary producers fix between 10 -12 Gt of dissolved carbon dioxide into particulate organic carbon a year and transfer them to the deep interior (Henson et al., 2012; Stewart et al., 2010).

In the open ocean, primary production is typically limited by the availability of major nutrients such as N and P, or trace metals such as Fe. The concentration of these elements is generally dependent on the efficiency of the recycling among microorganisms (Verdeny et al., 2008). Most oligotrophic ocean environments are dependent on these recycled nutrients and only a small fraction is affected by the input of “new” nutrient material either by upwelling processes or atmospheric deposition (Verdeny et al., 2008). Therefore, the amount of biologically fixed carbon that is capable of being sequestered from the atmosphere to the deep ocean is largely dependent on the availability of nutrients in the eutrophic zone of the water column, driving the

biological production and the amount lost due to remineralization. The ratio of Net Primary Productivity (NPP) and the amount of POC exiting the euphotic zone represents the efficiency of the biological pump.

### 3.1.1 Estimating POC Flux

POC export from the surface ocean layers is studied in the marine environment by various techniques. Direct measurement of POC flux is possible with sediment traps (Owens et al., 2013). Sediment traps styles vary and may be moored to the sea floor or free drifting. Particle Interceptor Traps (PITs) are drifting sediment traps and are effective as they minimize the effect of currents (Buesseler et al., 2000). Indirect measurement of vertical flux can also be obtained using natural radioisotope methods with $^{210}$Po (Friedrich et al., 2002) and $^{234}$Th (Buesseler et al., 2001). Scavenging of $^{234}$Th and $^{210}$Po by sinking particles disrupts the parent-daughter secular equilibrium and results in the difference of their activity which gives the estimate of particle flux. Depending on the half-lives of the isotopes, they represent particle flux integrated over different time scales. $^{210}$Po provides a flux rate integrated over several months ($t_{1/2}$=138.3 d), while $^{234}$Th represents a flux rate integrated over a few weeks ($t_{1/2}$=24 d). The carbon export of the open ocean is a major focus of oceanographic studies in the world's oceans. Data sets on POC fluxes are extremely limited for the Gulf of Mexico.

In present work, $^{210}$Po and $^{210}$Pb disequilibria are used to estimate POC fluxes from the euphotic zone in the northern Gulf of Mexico along a north south transect starting on the continental shelf near the mouth of the Atchafalaya River to the continental slope region.

$^{210}$Po ($t_{1/2}$=138.3 d) is a part of the naturally occurring $^{238}$U decay chain and is produced by the decay of its grandparent $^{210}$Pb ($t_{1/2}$=22.3 y) via decay of $^{210}$Bi ($t_{1/2}$=5.012 d). $^{210}$Po in the marine environment is almost exclusively supplied by the in situ decay of its grandparent $^{210}$Pb, which is delivered by the in situ decay of its longer-lived grandparent $^{226}$Ra, and from atmospheric deposition (Friedrich et al., 2002).

$^{210}$Pb and $^{210}$Po are both particle reactive but have different particle affinities and binding mechanisms. $^{210}$Pb quickly absorbs to all sedimentary particle surfaces, whereas $^{210}$Po becomes incorporated via biological activity into the cytoplasm and cell wall of some species of phytoplankton (Fisher et al., 1983). The partitioning of $^{210}$Po in biological material is similar to that of protein and sulfur within the cell (Fisher et al, 1983; Stewart and Fisher, 2003a, 2003b). Due to the stronger bioaccumulation of $^{210}$Po in organic matter relative to $^{210}$Pb, $^{210}$Po is more efficiently recycled during particle remineralization and thus is characterized by a longer residence time in the water column than $^{210}$Pb.

The biogeochemical differences between $^{210}$Pb and $^{210}$Po result in $^{210}$Po being more efficiently removed from surface waters than $^{210}$Pb, via scavenging by sinking particles (Hong et al., 2013; Verdeny et al., 2008). Since $^{210}$Po has a higher affinity than $^{210}$Pb for organic particles, a deficit of $^{210}$Po is usually produced in the upper water column due to sinking biological material. This activity deficit between $^{210}$Po and its long-lived parent $^{210}$Pb in the water column is caused by the scavenging onto sinking particles and the utilization of $^{210}$Po and $^{210}$Pb to determine particle flux in the open ocean has been demonstrated in various studies. This method is widely used but to our

knowledge has never been applied to the northern Gulf of Mexico, where there is very little measurement of POC flux from the upper ocean.

Primary Productivity in the northern Gulf of Mexico is largely driven by the input of anthropogenic nutrients from the Mississippi River. Surface waters of the central Gulf of Mexico show a well-defined seasonal cycle in phytoplankton pigment concentration (Biggs et al., 2008). The summer NPP maxima are associated with the Mississippi River water transported offshore to the east and southward by anticyclonic eddies in the NE Gulf. Also, average monthly NPP concentrations in June-August in the Gulf of Mexico are generally 50% higher than in November-February (Biggs et al., 2008). However, available POC flux data in the Gulf of Mexico is not extensive. Biggs et al. (2010) estimated POC fluxes to the seafloor in the Gulf of Mexico to range from 9-18 mg C $m^{-2}$ $day^{-1}$, using a remote-sensing approach. Hung et al. (2010) used sediment traps to estimate the POC fluxes in the upper water column (~150m) in the Northern Gulf of Mexico to range from 49-116 mg C $m^{-2}$ $d^{-1}$. There are disadvantages to these methods however. A remote sensing approach relies heavily on major assumptions and only calculates the NPP directly on the surface and using a mathematical model relates that to POC flux estimate. Sediment trap methods can also be very time consuming and costly and do not take into account the effect of swimmers and currents into POC flux estimations. Therefore, a radioisotope disequilibria method is ideal when calculating the POC flux in an open ocean environment.

## 3.2 Methodology

### 3.2.1 Sample Collection

Water column profiles were collected from six stations along a sampling transect in the Northern Gulf of Mexico during August 2011. August represents the period of lowest NPP in the Gulf of Mexico (Biggs et al., 2008). Since, NPP is the highest in March/April and goes to its lowest point in August, averaging the NPP for the six months prior to August provides a representative average of NPP for the year. $^{210}$Po is a favorable radiochemical proxy to use in this aspect because of its decay properties ($t_{1/2}$=138.3 d). The half-life of $^{210}$Po offers a seasonal perspective to this method by integrating the POC export over the past 6-8 months.

The sampling transect for this study runs North to South and begins approximately 150 km south of the mouth of the Atchafalaya river and extends across the Louisiana/Texas continental slope, with a total transect distance of approximately 220 km (Figure 3.1). We collected samples at two coastal stations, in shallow water, located on the continental shelf, C1 and C2. The other four stations, S1-S4, are located on the slope of the Louisiana/Texas continental shelf and extend south into the Gulf of Mexico interior. Stations are arranged based on proximity to the shore line and are shown in Figure 3.1. Sample collection dates and location are shown in Table 3.1.

Water column samples, consisting of 8-10 L of seawater, were collected via ship rosette system to determine the total $^{210}$Po and $^{210}$Pb activity in the water column at each station. Particulate matter samples were collected using large volume in-situ

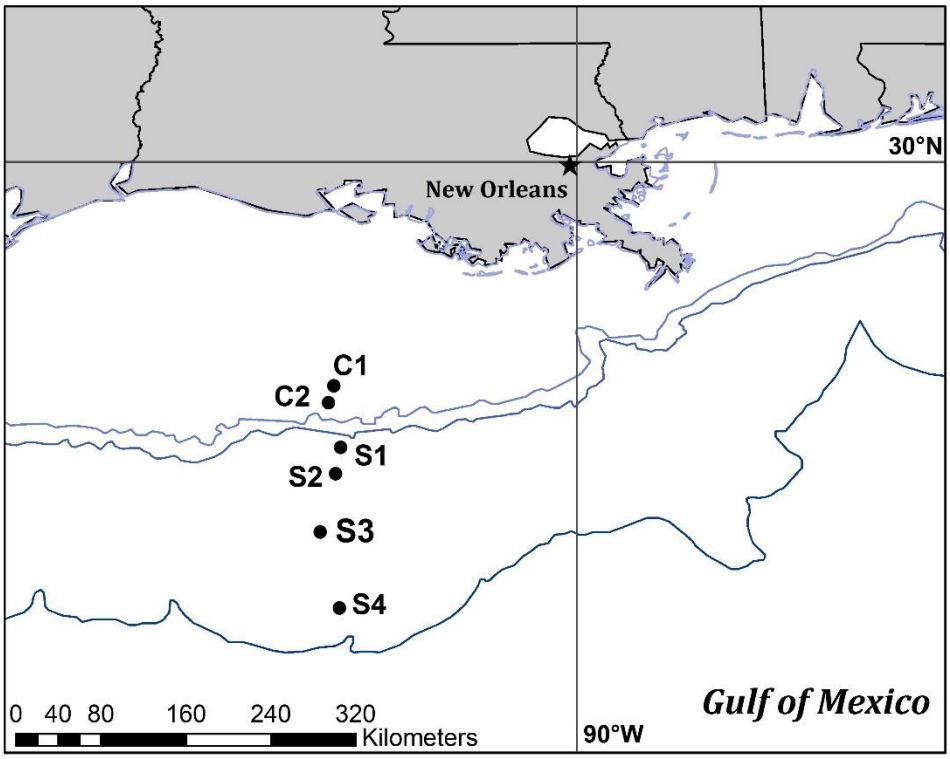


Figure 3.1 Sample collection locations on the Gulf of Mexico continental shelf and shelf slope. All stations lie on a transect south of the mouth of the Atchafalaya River. Samples collected in August 2011. C1 and C2 are coastal stations, S1, S2, S3, and S4 are shelf slope stations. Bathymetric lines represent 500 m depth intervals.

Table 3.1 Sample collection date and location for all stations

| ID | Latitude | Longitude | Date |
|---|---|---|---|
| C1 | 28.1025 | -92.05662 | 8/6/2011 |
| C2 | 27.93443 | -92.10167 | 8/12/2011 |
| S1 | 27.5816 | -91.99943 | 8/10/2011 |
| S2 | 27.35793 | -92.04197 | 8/11/2011 |
| S3 | 26.86525 | -92.17098 | 8/8/2011 |
| S4 | 26.2205 | -92.00855 | 8/9/2011 |

pumps which filtered approximately 900 L of seawater at various depths within the water column to determine POC concentration and particulate $^{210}$Po and $^{210}$Pb. Sediment cores, used to determine the $^{210}$Pb inventory of sediments, were collected at some stations using a multicorer.

### 3.2.2 Analytical Methods

#### 3.2.2.1 Water Samples

Total activity of $^{210}$Po and $^{210}$Pb in the water column was measured from 8-10 liters of unfiltered seawater, collected via ship rosette system. Water samples were transferred to acid-cleaned polycarbonate containers and acidified with concentrated HCl to pH 1-2. Samples were then spiked with known amounts of $^{209}$Po and stable $Pb^{2+}$ yield monitors to quantify any subsequent losses of Po and Pb. A $Fe^{3+}$ co-precipitate was also added (30 mg) to each sample and after an equilibration period of 6-8 hours, the pH was brought back up to approximately pH 8-8.5, using concentrated $NH_4OH$. Samples were allowed to precipitate and settle for 8-10 hours. The precipitate was then transferred to 1 L polypropylene bottles. One-liter bottles were stored on board for later processing in the laboratory at Louisiana State University. Precipitate was dissolved using concentrated HCl and reconstituted to 1M HCl. The $^{210}$Po analytical methods used to determine $^{210}$Po activity in the water column are similar to those described in Nozaki (1986) and Masque et al (2002).

#### 3.2.2.2 Particulate Samples

Particulate $^{210}$Po activity, $^{210}$Pb activity and POC concentrations in the water column were measured using in-situ pumps deployed at various depths. Pumps filtered seawater through 51 µm screens followed by 1 µm quartz microfiber filters. Material on screens was transferred to smaller 1 µm quartz microfiber filters. A subset was taken from each quartz microfiber filter and analyzed for POC concentration using a Perkin Elmer Series II CHNS/O 2400 Analyzer. Another subset of the quartz microfiber filters were spiked with known quantities of $^{209}$Po to quantify any subsequent loss of polonium

and to monitor method efficiency. Spiked filters were then digested in a solution of HCl, $HNO_3$, and HF via a MARS microwave digestion chamber system. The sampling solution was evaporated and reconstituted with 1M HCl.

3.2.2.3 Alpha Spectroscopy

Silver planchets were suspended in sampling solutions for both particulate matter and bulk water samples and Polonium was auto-deposited directly on to silver planchets following methods described by Flynn (1968) and Fleer and Bacon (1984). After the initial plating of Polonium onto the silver planchets was complete, a 1 mL aliquot was extracted directly from the sample and these aliquots were used to determine the yield of $^{210}Pb$ by measuring the $Pb^{2+}$ via ICP-OES. The plating solution were then cleaned of all residual Polonium remaining using an AGX-I resin column, re-spiked with $^{209}Po$ yield tracer and stored for 9-10 months, allowing $^{210}Po$ to be regenerated from the decay of $^{210}Pb$. This freshly produced $^{210}Po$ represented the concentration of $^{210}Pb$ in the original sample (Swarzenski, 1999). This analysis yields the total $^{210}Po$ and $^{210}Pb$ activity in the water column. The silver planchets used to measure both $^{210}Po$ and $^{210}Pb$ were then counted on Canberra Alpha Analyst high-resolution silicon-surface barrier (PIPS) alpha detectors. All decay and volume corrections for $^{210}Po$ and $^{210}Pb$ quantification were derived from Church et al. (2012) and Baskaran et al. (2012).

3.2.2.4 Sediment Cores

Sediment Cores were collected via a multicorer system and sliced into 1 cm sections. Porosity was determined in each core using the wet-dry weight method. $^{210}Pb$ concentration was measured in each core segment using a Canberra Gamma Well Detector system.

#### 3.2.2.5 Net Primary Productivity Calculation

Ocean net primary production (NPP) for the 6 station locations was determined from the Moderate Resolution Imaging Spectroradiometer (MODIS) ocean color satellite sensor data using the Vertically Generalized Production Model (VGPM) (Behrenfeld and Falkowski 1997). NPP data were derived from MODIS at 1/12 degree resolution.

#### 3.2.2.6 Flux Calculations

The integrated $^{210}$Po flux in the water column was calculated following methods by Verdeny et al. (2008) and was determined using:

$$F_{Po} = \sum \int (A_{Pb} - A_{Po}) \lambda_{Po} dz$$

Where $F_{po}$ is the $^{210}$Po flux, $A_{Pb}$ is the $^{210}$Pb activity in the water column, $A_{Po}$ is the $^{210}$Po activity in the water column, $\lambda_{Po}$ is the $^{210}$Po decay constant, and dz is the integrated thickness of the water column layer. Steady-state POC flux calculated from $^{210}$Po deficit in the water column requires knowledge of the C/$^{210}$Po ratio in sinking particles. The $^{210}$Po flux at each station was multiplied by the C/$^{210}$Po ratio in particulate matter in the water column at each station to yield the overall POC flux.

## 3.3 Results and Discussion

### 3.3.1 POC Fluxes

#### 3.3.1.1 Coastal Stations

Stations C1 and C2, the coastal stations, are much shallower in depth than the four shelf stations and are therefore much different hydrographically. Both stations show a nepheloid layer near the bottom and indicated sediment resuspension based on elevated beam attenuation in the lower water column (Figure 3.2). Resuspension of particulate matter will alter the $^{210}$Pb – $^{210}$Po based flux measurement and give an erroneous estimate of POC flux. Therefore, at C1 and C2, we calculated POC fluxes at

a shallower depth of 60m, above the nepheloid layer of resuspended material. These flux estimates, however, does not reflect the export from the entire water column. In C1 and C2, dissolved $^{210}$Po is deficient relative to $^{210}$Pb in the upper water column (Fig. 3.3). This is expected based on the parent-daughter relationship of this radioisotope pair and the affinity for organic matter of $^{210}$Po. In the lower water column layers of both profiles, they approach equilibrium.

The C/$^{210}$Po ratio for C1 and C2 were 4.47 and 7.36, respectively. $^{210}$Po fluxes were 6.9±0.65 dpm $m^{-2}$ $d^{-1}$ and 3.81±0.35 dpm $m^{-2}$ $d^{-1}$ at C1 and C2, respectively (Table 3.2). Corresponding POC fluxes were 22.6±2.5 mg C $m^{-2}$ $d^{-1}$ and 28.05±3.7 mg C $m^{-2}$ $d^{-1}$ for C1 and C2, respectively.

3.3.1.2 Slope Stations

Stations S1, S2, S3 and S4 are located on the slope the continental slope and are considerably deeper that the coastal stations (Fig. 3.1). Due to the greatly increased depth at these stations, there is minimal interference in the water column from resuspended particles in the euphotic zone (Fig. 3.2). In all shelf profiles, there is an increase in chlorophyll concentration (fluorescence) around the 100m depth (Fig. 3.2). Beam attenuation at S1-S4 also shows that the water column is generally void of excess particles. The $^{210}$Po concentration throughout the water column of all slope stations is generally deficient relative to $^{210}$Pb concentration (Fig. 3.3). This is not true for stations S3 and S4, in which $^{210}$Po concentration exceeds $^{210}$Pb concentration for two depths. This increase is likely a result of extensive organic matter remineralization at those depths.

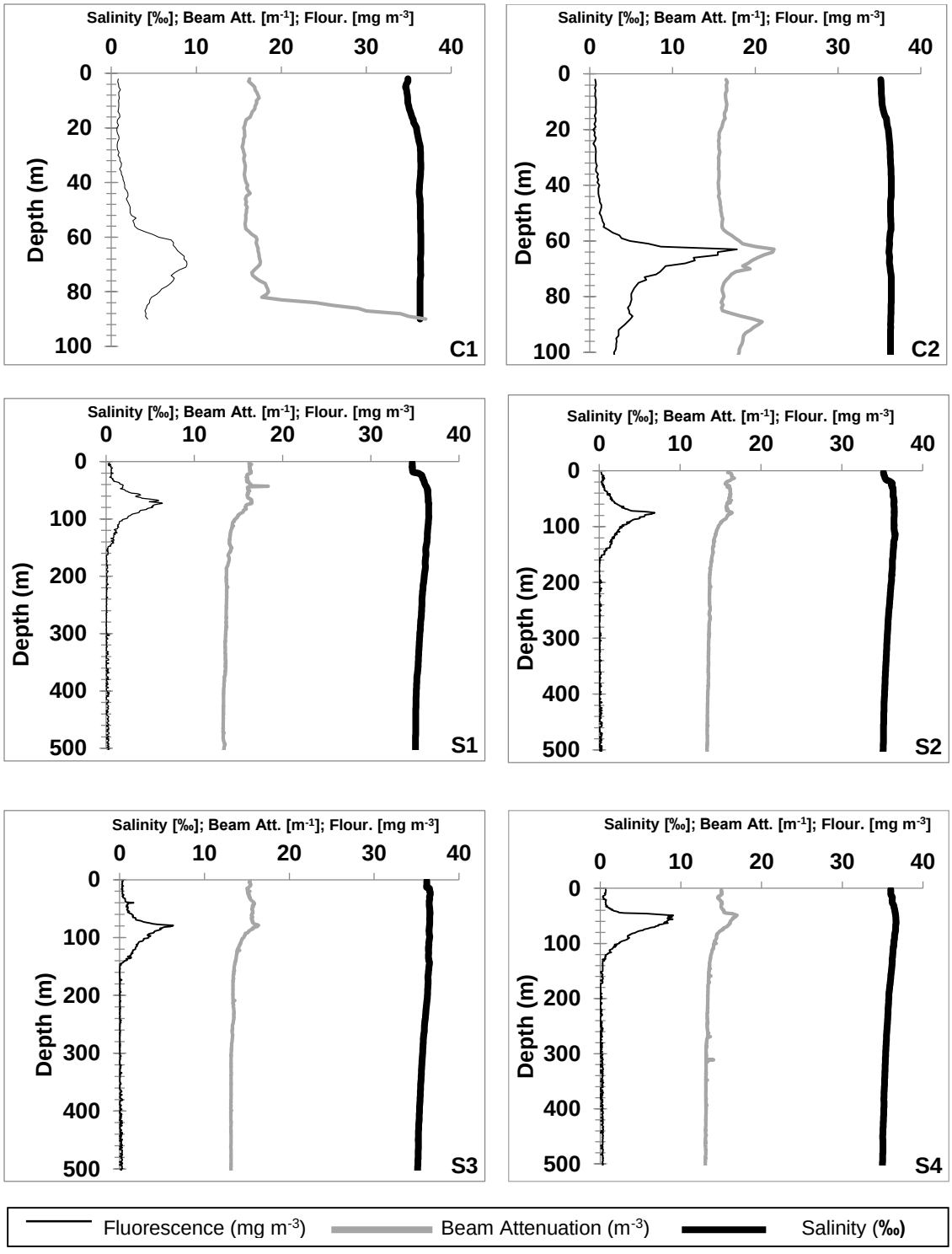


Figure 3.2 Water column profiles showing Salinity, Beam Attenuation, and Fluorescence in the water column. Beam attenuation and Fluorescence values have been magnified 50 times and 10 times, respectively, so that all values can be shown on the same scale.

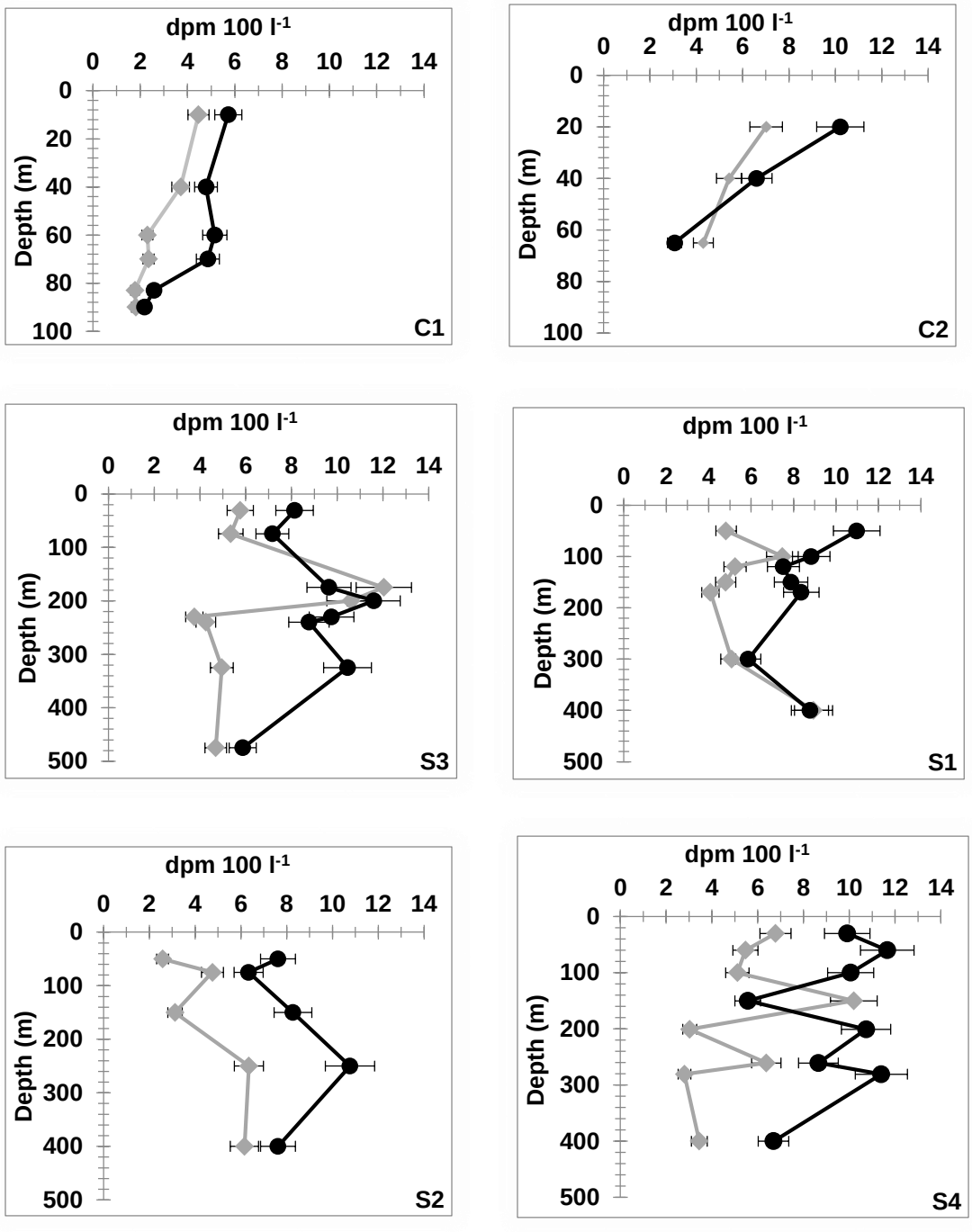


Figure 3.3 Total $^{210}$Po and $^{210}$Pb activity in the water column.

Table 3.2 Total water depth, C/$^{210}$Po, $^{210}$Po flux and POC flux for all six sample stations. POC flux is measured at the 60 m depth for C1 and C2 and the 150 m depth for S1, S2, S3, and S4.

| ID | Water Depth | C/$^{210}$Po | $^{210}$Po flux | POC flux |
|---|---|---|---|---|
| | m | mg/dpm | dpm/m$^2$/day | mg/m$^2$/day |
| C1 | 90 | 4.47 | 5.06 | 22.60 |
| C2 | 164 | 7.36 | 3.81 | 28.05 |
| S1 | 984 | 2.4 | 30.7 | 75.3 |
| S2 | 1104 | 2.9 | 29.4 | 85.6 |
| S3 | 1017 | 1.06 | 9.85 | 10.45 |
| S4 | 2209 | 0.66 | 23.3 | 15.4 |

The $^{210}$Po and POC fluxes (Table 3.2) were measured at a depth of 150m, just below the euphotic zone in order to account for all material exiting the euphotic zone. The C/$^{210}$Po ratio ranged from 2.9 to 0.66. The $^{210}$Po flux was greatest near the shore at station S1 and was measured at 30.7±3.1 dpm m$^{-2}$ d$^{-1}$. The lowest $^{210}$Po was measured at station S3 and was 9.85±0.99 dpm m$^{-2}$ d$^{-1}$. POC flux for the shelf stations was greater closer to the shore, in areas of higher primary productivity, and followed a general trend of decreasing as the transect moved further from shore. The highest POC flux was 85.6±7.6 mg C m$^{-2}$ d$^{-1}$ at station S2 and the lowest POC flux was 10.4±1.1 mg C m$^{-2}$ d$^{-1}$ at S3.

### 3.3.2 Sediment Focusing

Knowing the fate of sinking particles in the water column can be determined utilizing a sediment focusing approach. Due to the strong particle affinity of $^{210}$Pb, comparing the $^{210}$Pb inventory in the water column and sediment directly below provide insight on the fate of sinking particles within the water column. This approach determines if particles are being deposited from more shallow regions or being transported laterally within the water column. The deficiency of $^{210}$Pb between its supply (dpm m$^{-2}$) and measured inventory (dpm m$^{-2}$) in the water column is a measure of either

the scavenging intensity or lateral transport in a given site (Baskaran and Santschi, 2002). A comparison of the intensity production rate of $^{210}$Pb to its flux, derived from sediment inventory, enables the investigation of sediment focusing and/or boundary scavenging of $^{210}$Pb. The calculated and expected $^{210}$Pb inventories in the water column and sediment were determined at some stations. Calculated $^{210}$Pb inventories were determined from sediment cores. The expected $^{210}$Pb inventory in the water column was calculated as follows:

$$^{210}Pb_{ex}\ inventory = [(A_{226Ra} - A_{210Pb})*\lambda_{Pb}*z + A_{210Pbatm}]*\tau_{Pb}$$

Where $A_{226Ra}$ is the $^{226}$Ra water column activity. This value is taken from Krest et al. (1999). $^{226}$Ra activity is assumed to be equal throughout the ocean water column due to the long half-life of this radioisotope. $A_{210Pb}$ is the $^{210}$Pb water column activity, measured at stations along the transect. $A_{210Pbatm}$ is the activity of atmospheric $^{210}$Pb deposited into the water column. This value was taken from Baskaran and Santschi (2002). $\lambda_{Pb}$ is the $^{210}$Pb decay constant, $\tau_{Pb}$ is the mean life of $^{210}$Pb (32.1 years) and z is the depth of the water column. Lateral transport of sediment or areas of sediment accumulation were determined by calculating the F ratio as follows:

$$F = (^{210}Pb_{excess\ in\ water\ column})/(^{210}Pb_{exess\ in\ sediment\ core})$$

F<1 indicates the $^{210}$Pb inventory is greater in the sediment on the ocean floor than can be supplied by vertical flux from the water column. This suggests more sediment is accumulating on the ocean floor than is present in the water column and therefore represents an area of sediment accumulation. F>1 indicates less $^{210}$Pb is reaching the sediment compared to what is available in the water, suggesting lateral transport of particles within the water column.

The $^{210}$Pb excess inventory of each sediment core and the integrated $^{210}$Pb inventory in the water column are shown in Figure 3.4 and values are shown in Table 3.3. For stations C1 and C2, the same sediment core was used due to the proximity of the stations to the core. The expected $^{210}$Pb inventory is 193.66 dpm mg$^{-3}$ and 193.3 dpm mg$^{-3}$ in C1 and C2, respectively. The calculated $^{210}$Pb inventory was 177.37 dpm mg$^{-3}$ at C1 and C2. In both, the calculated $^{210}$Pb inventory is within error of the expected $^{210}$Pb inventory in the water column (F=1). This suggests that this is not an area of lateral transport or sediment focusing but rather a zone where sediments are efficiently reaching the seafloor and no sediments are being supplied from a lateral source.

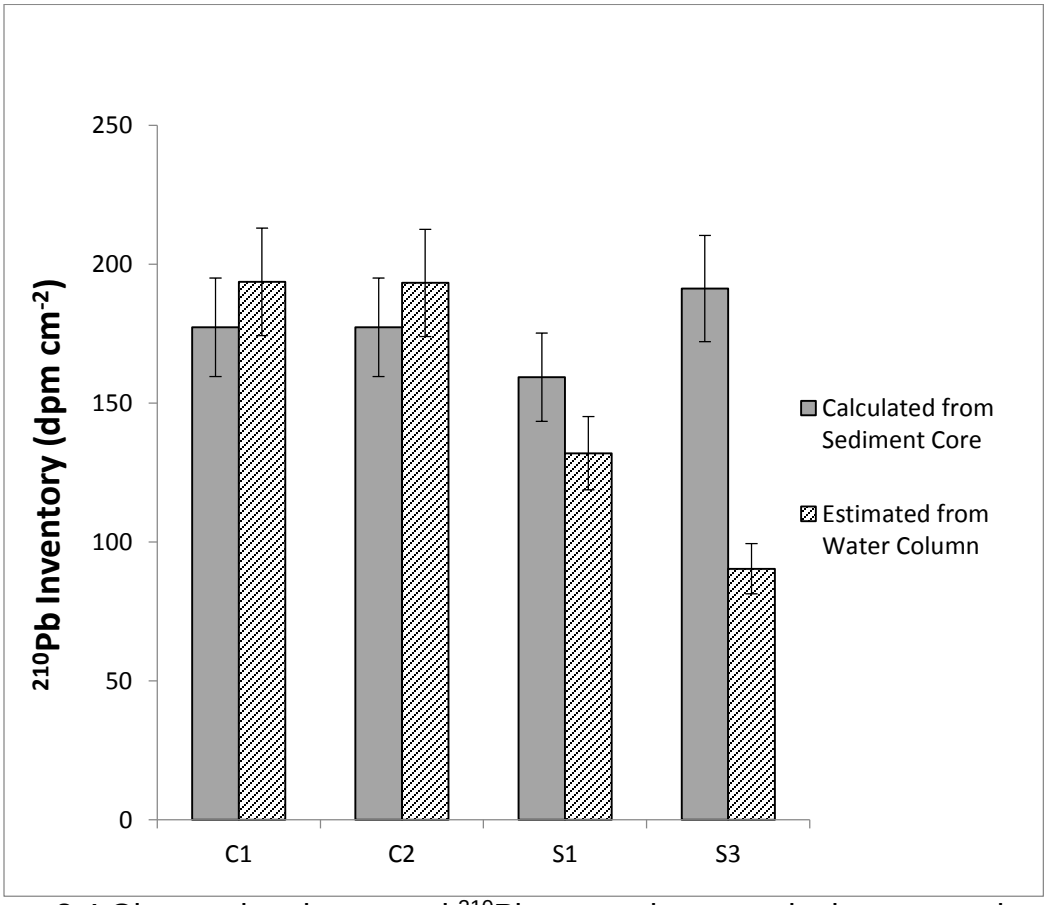


Figure 3.4 Observed and expected $^{210}$Pb excess inventory in the water column and sediment two coastal stations and two slope stations.

At stations S1 and S3 the calculated inventory of $^{210}$Pb is 159.35 dpm mg$^{-3}$ and 131.95 dpm mg$^{-3}$, respectively. The expected $^{210}$Pb inventory was 131.95 dpm mg$^{-3}$ and 90.39 dpm mg$^{-3}$ for S1 and S2, respectively. For both slope stations, the $^{210}$Pb inventory in the sediment core is greater than the inventory of $^{210}$Pb found in the water column (F<1). This suggests that this is an area of sediment focusing and material is being deposited from a lateral source. Sediment is potentially being transported to the deep gulf within the water column on the continental slope. Similar transport of particulate carbon in the northern Gulf of Mexico has also been hypothesized by Rowe et al. (2008) based on high Sediment Community Oxygen Consumption (SCOC) on the seafloor that cannot be balanced by estimates of POC reaching the seafloor.

Table 3.3 Water column and sediment $^{210}$Pb excess inventory at select stations.

| **ID** | **Water $^{210}$Pb inventory** | **Sediment $^{210}$Pb Inventory** |
|---|---|---|
| | **dpm/mg$^3$** | **dpm/mg$^3$** |
| C1 | 193.66 | 177.37 |
| C2 | 193.30 | 177.37 |
| S1 | 131.95 | 159.35 |
| S2 | *N/D* | *N/D* |
| S3 | 90.39 | 191.28 |
| S4 | *N/D* | *N/D* |

3.4 Discussion

NPP in surface water at all stations is shown in Table 3.4 and is highest near the shore and decreases south into the Gulf of Mexico. This gradient is expected due to the proximity of the primary source of nutrient to the area, the Mississippi and Atchafalaya Rivers. The POC fluxes of shelf stations (S1-S4) decreases in a similar gradient to NPP. This does not hold absolutely true for our C flux values at individual stations but the trend shows a general decrease that is within error. Table 3.4 shows the POC flux efficiency based on NPP and measured POC fluxes. The POC flux efficiencies

Table 3.4 POC flux, Primary productivity and POC flux efficiency for all six stations.

| ID | POC flux | NPP | Export Efficiency |
|---|---|---|---|
| | mg/m$^2$/day | mg/m$^2$/day | % |
| C1 | 22.60 | 526.79 | 4.28 |
| C2 | 28.05 | 492.06 | 5.70 |
| S1 | 75.3 | 430.72 | 17.48 |
| S2 | 85.6 | 393.16 | 21.77 |
| S3 | 10.45 | 370.57 | 2.81 |
| S4 | 15.4 | 355.88 | 4.32 |

for 2011 ranged from 4.29% to 21.77%. The biological pump appears to be more efficient closer to the shore, likely as a result of higher nutrient availability at the stations closer to shore.

POC flux at the two shallow coastal stations (C1 and C2) should be treated with caution and may be an underestimation since fluxes were calculated at a shallow depth, 60 m, in order to avoid interference from bottom resuspension. Conversely, S1-S4, are located in much deeper sections of the Gulf of Mexico and are not affected by particles from other sources in the water column. POC flux efficiencies range from 4% and 21% for shelf stations. Based on the NPP gradient, this suggests more nutrients are available to stations closer to the shore and thus POC is more efficiently exported out of the euphotic zone. At stations further from shore, however, POC export efficiency and NPP are lower. This suggests that in these areas, more POC is recycled or less POC is available in the upper ocean and thus less material is exported out of the euphotic zone. The POC flux efficiencies calculated are similar to POC flux efficiency values reported by Rocha and Passow (2007), who calculated an average POC flux of 15% in the Gulf of Mexico. This study indicates that as the system transitions from a productive nutrient rich zone to oligotrophic nutrient starved area the recycling of organic matter becomes more efficient. Our data also shows that there is regional variability in the amount of

sediment sinking to the bottom relative to the amount of material in the water column. Thus remote-sensing based POC fluxes may not be a good indicator of POC fluxes reaching the seafloor immediately below.

# CHAPTER 4: CONCLUSION AND SUMMARY

The overall goal of this research was to examine $^{210}$Po dynamics in the Northern Gulf of Mexico by measuring $^{210}$Po remobilization from hypoxic sediments and analyzing POC export from the euphotic zone in the upper ocean by utilizing the $^{210}$Pb - $^{210}$Po disequilibria method. The Northern Gulf of Mexico is characterized by one of the largest seasonal hypoxic zones in the world and is constantly affected by the input of nutrient, biological material, and other sedimentary particles by the Mississippi and Atchafalaya Rivers.

Chapter two is focused on $^{210}$Po remobilization from hypoxic sediments in the northern Gulf of Mexico. $^{210}$Po was found to be enriched in bottom waters by as much as 50% compared to surface waters and the $^{210}$Pb/$^{210}$Po ratio was below 1 in the lower water column layers for most sample stations, indicating a bottom source of $^{210}$Po. The relationship between $^{210}$Po remobilization and low dissolved oxygen in the water column is not straightforward and rather complicated. Though low-oxygen in the water column is associated with $^{210}$Po remobilization, this data shows that there are likely other mechanisms that are driving this process. We did not see a strong correlation with the degree of hypoxia and the rate of remobilization. $^{210}$Po remobilization is likely a product of two processes; Fe and Mn cycling in the low oxygen water column and release as a result of the degradation of organic matter. Several studies have shown that Fe and Mn cycling in the low oxygen water column are associated with $^{210}$Pb and $^{210}$Po remobilization, respectively (Benoit and Hemond, 1990). Dissolved Mn in water column profiles from some stations in 2011 show a strong correlation with $^{210}$Po activity in the lower water column. This is the first study showing $^{210}$Po remobilization in a low-oxygen

marine environment. Future projects on $^{210}$Po remobilization should include a benthic flux chamber deployed to the sediment surface to monitor the rate of $^{210}$Po remobilization over time. Ideally the chamber should measure the flux rate of redox sensitive metals such as Fe and Mn being released from the sediment as well. Though this data is the first to show $^{210}$Po release from low oxygen sediments in a marine environment, more research must be done to better understand the behavior and release mechanism of $^{210}$Po from sediments in a coastal system.

The major research focus of chapter 3 is to estimate POC fluxes using the $^{210}$Pb – $^{210}$Po disequilibria along a north south transect near the mouth of the Atchafalaya River. POC flux was determined at C1 and C2 for the top 60 m of the water column due to interference from resuspended particles. These POC flux estimates from the coastal stations are likely an underestimate of the total POC leaving the total euphotic zone. At slope stations, S1-S4, POC fluxes were estimated at 150m and were generally higher closer to the shore, likely as a result of the higher NPP. POC flux and NPP showed a similar gradient in the northern Gulf of Mexico based on distance from the shore. $^{210}$Pb excess inventories of sediment cores and the water column suggest sediment focusing in stations located on the continental slope, suggesting material is being transported to the deep gulf within the water column on the continental slope. POC flux efficiency was greater closer to the shore, suggesting POC is recycled in the upper ocean more further from the shore. Closer to shore POC is exported from the euphotic zone more efficiently. The higher export efficiency close to shore is likely as result of higher nutrient availability, sloppy feeding by zooplankton and export of POC via fecal pellets. Therefore, this data suggests there is a transition zone on the slope of the continental

shelf between a nutrient rich euphotic zone and oligotrophic nutrient starved zone, where POC is recycled in the upper ocean. POC flux measurements using the $^{210}$Pb - $^{210}$Po disequilibria have never been done in the northern Gulf of Mexico and this dataset indicates it can be applied successfully in this region to understand the carbon flux and efficiency of the biological pump.

# REFERENCES


Balisterieri, L.S., Murray, J.W. and Paul, B., 1995. The geochemical cycling of stable Pb, $^{210}$Pb, and $^{210}$Po in seasonally anoxic Lake Sammamish, WA. Geochemical Cosmochemica Acta, 59: 4845-4861.

Baskaran, M., Church, T., Hong, G.H., Kumar,A., Qiang, M., Choi, H., Riguad, S. and Maiti, K., 2012. Effects of flow rates and composition of the filter, and decay/in-growth correction factors involved with the determination of in-situ particulate $^{210}$Po and $^{210}$Pb in seawater. Limnology and Oceanography: Methods.

Baskaran, M. and Santschi, P.H., 2002. Particulate and dissolved $^{210}$Pb activities in the shelf and slope regions of the Gulf of Mexico waters. Continental Shelf Research, 22: 1493-1510.

Biggs, D.C., Hu, C. and Muller-Karger, F.E., 2008. Remotely Sensed sea-surface chlorophyll and POC flux at Deep Gulf of Mexico Benthos sampling stations. Deep-Sea Research II, 55: 2555-2562.

Behrenfeld, M. J., and P. G. Falkowski. 1997. A consumer's guide to phytoplankton primary productivity models. Limnology and Oceanography **42:** 1479-1491.

Benoit, G. and H. F. Hemond., 1990. $^{210}$Po and $^{210}$Pb Remobilization from Lake Sediments in Relation to Iron and Manganese Cycling. Environmental Science Technology, 24: 1224-1234.

Bianchi, T.S., DiMarco, S.F., Cowan Jr, J.H., Hetland, R.D., Chapman, P., Day, J.H. and Allison, M.A. 2010. The Science of Hypoxia in the Northern Gulf of Mexico. Science of the Total Environment, 408: 1471-1484.

Buesseler, K.O. Steinberg, D.K., Michaels, A.F., Johnson, R.J., Andrews, J.E., Valdes J.R., and Price J.F., 2000. A comparison of the quantity and composition of material caught in a neutrally buoyant versus surface-tethered sediment trap. Deep-Sea Research I, 47: 277-294.

Bustamante, P., Germain, P., Leclerc, G. and Miramand, P., 2002. Concentration and distribution of $^{210}$Po in the tissues of the scallop Chlamys varia and the mussel Mytilus edulis from the coasts of Charente-Maritime (France). Marine Pollution Bulletin, 44: 997-1002.

Cherry, R. D., 1964. Alpha Radioactivity of Plankton. Nature, 203: 139-143.

Cherry, R. D. and M. Heyraud., 1981. Polonium-210 content of marine shrimp; Variation with biological and environmental factors. Marine Biology, 65: 165-175.

Church, T., Riguad, S., Baskaran, M., Kumar, A., Friedrich, J., Masque, P., Puigcorbe, V., Kim,G., Radacovich, O., Hong G., Choi, H., and Stewart, G., 2012. Intercalibration studies of $^{210}$Po and $^{210}$Pb in dissolved and particulate seawater samples. Limnology and Oceanography: Methods, 10: 776-789.

Clulow, F.V., Dave, N.K., Lim, T.P. and Avadhanula, R., 1998. Radionuclides (lead-210, polonium-210, thorium-234, and -232) and thorium and uranium in water, sediments and fish from lakes near the city of Elliot Lake, Ontario, Canada. Environmental Pollution 99: 199-213.

Cochran, J.K., Bacon, M.P., Krishnaswami, S. and Turekian, K.K., 1983. $^{210}$Po and $^{210}$Pb distributions in the central and eastern Indian Ocean. Earth and Planetary Science Letters, 65(2): 433-452.

Fisher, N.S., Burns, K.A., Cherry, R.D. and Heyraud, M., 1983. Accumulation and cellular distribution of $^{241}$Am, $^{210}$Po, and $^{210}$Pb in two marine algae. Marine Ecology, 11: 233-237.

Fisher, N.S. and J.R. Reinfelder., 1995. The trophic transfer of metals in marine systems. p. 1193-1201. *In* Stewart, G. M. and N. S. Fisher., 2003. Experimental studies on the accumulation of polonium-210 by marine phytoplankton. Limnology and Oceanography, 48(3): 1193-1201.

Fisher, N.S., Burns, K.A., Cherry, R.D. and Heyraud, M., 1983. Accumulation and cellular distribution of $^{241}$Am, $^{210}$Po, and $^{210}$Pb in two marine algae. Marine Ecology, 11: 233-237.

Fleer, A.P. and Bacon, M.P., 1984. The determination of $^{210}$Pb and $^{210}$Po in seawater and marine particulate matter Nuclear Instruments and Methods in Physics Research 223(2): 243-249.

Flynn, W.W., 1968. The determination of low levels of $^{210}$Po in environmental samples. Anal. Chim. Acta., 43: 221-227.

Friedrich, J. and M. M. R. v. d. Loeff., 2002. A two-tracer ($^{210}$Po-$^{234}$Th) approach to distinguish organic carbon and biogenic silica export flux in the Antarctic Circumpolar Current. Deep Sea Research I, 49: 101-120.

Germain, P., Leclerc, G. and Simon, S., 1995. Transfer of polonium-210 into Mytillius edulis (L.) and Fucus vesiculosus (L.) from Bane de Seine (Channel coast of France). Science of the Total Environment, 164: 109-123.

Harada, K., Burnett, W.C. and LaRock, P.A., 1989. Polonium in Florida groundwater and its possible relationship to the sulfer cycle and bacteria. Geochimica et Cosmochimica Acta, 53: 143-150.

Henson, S.A., Sanders, R. and Madsen, E., 2012. Global patterns in efficiency of particulate organic carbon export and transfer to the deep ocean. Global Biogeochemical Cycles, 26.

Hong, G.H., Baskaran, M., Church, T.M. and Conte, M., 2013. Scavenging, cycling and removal fluxes of $^{210}$Po and $^{210}$Pb at the Bermuda time-series study site. Deep-Sea Research II, 93: 108-118.

Hong, G.-H., S.-K. Park, M. Baskaran, S.H. Kim, C.S. Chung, and Lee, S.H., 1999. Lead-210 and poloniun-210 in the winter well-mixed turbid waters in the mouth of the Yellow Sea. Continental Shelf Research, 19: 1049-1064.

Honjo, S., Manganini, S.J., Krishfiend, R.A. and Francois, R., 2008. Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983. Progress in Oceanography, 76: 217-285.

Kim, G., Kim, S.-J., Harada, K., Schultz, M.K. and Burnett, W.C., 2005. Enrichment of Excess $^{210}$Po in Anoxic Ponds. Environmental Science Technology, 39: 4894-4899.

Krest, J.M., Moore, W.S. and Rama, 1999. $^{226}$Ra and $^{228}$Ra in the mixing zones of the Mississippi and Atchafalaya Rivers; indicators of groundwater input. Marine Chemistry, 64: 129-152.

Lee, C., Wakeham, S.G. and Hedges, J.I., 2000. Composition and flux of particulate amino acids anc chloropigments in equatorial Pacific seawater and sediments. Deep-Sea Research Part 1, 47: 1535-1568.

Masque, P., Sanchez-Cabeza, J.A., Bruach, J.M., Palacios, E. and Canals, M., 2002. Balance and residence times of $^{210}$Pb and $^{210}$Po in surface waters of the northwestern Mediterranean Sea. Continental Shelf Research 22: 2127-2146.

Moore, R.M. and Smith, J.N., 1986. Disequilibria between $^{226}$Ra, $^{210}$Pb, and $^{210}$Po in the Arctic Ocean and the implications for chemical modification of the Pacific water inflow. Earth and Planetary Science Letters, 77(3-4): 285-292.

Nieboer, E. and Richardson, D.H.S., 1980. The Replacement of the nondescript term 'heavy metals' by a biologically and chemically significant classification of metal ions. Environmental Pollution (Series B), 1: 3-26.

Nozaki, Y., 1986. $^{226}$Ra-$^{222}$Rn-$^{210}$Pb systematics in seawater near the bottom of the ocean. Earth and Planetary Science Letters, 80(1-2): 36-40.

Nozaki, Y., Dobashi, F., Kato, Y. and Yamamoto, Y., 1998. Distribution of Ra isotopes and the $^{210}$Pb and $^{210}$Po balance in surface seawaters of the mid Northern Hemisphere. Deep-Sea Research Part 1, 45: 1263-1284.

Nozaki, Y., Zhang, J. and Takeda, A., 1997. $^{210}$Pb and $^{210}$Po in the equatorial Pacific and Bering Sea: the effects of biological productivity and boundary scavenging. Deep-Sea Research Part II, 44(9-10): 2203-2220.

Owens, S.A., Buesseler, K.O., Lamborg, C.H., Valdes, J., Lomas, M.W., Johnson, R.J., Steinberg, D.K., and Siegel, D.A., 2013. A new time series of particle export from neutrally buoyant sediment traps at the Bermuda Atlantic Time-series Study site. Deep-Sea Research I, 172: 34-47.

Radakovitch, O., Cherry, R.D., Heyraud, M. and Heussner, S., 1997. Unusual $^{210}Po/^{210}Pb$ ratios in the surface water of the Gulf of Lions. Oceanologica Acta, 21(3): 459-468.

Reinfelder, J.R. and N.S. Fisher., 1991. The assimilation of elements ingested by marine ingested by marine copepods. Science, 251: 794-796.

Rocha, C.L.D.L. and Passow, U., 2007. Factors influencing the sinking of POC and the efficiency of the biological carbon pump. Deep-Sea Research II, 54: 639-658.

Rowe, G.T., Wei, C., Nunnally, C.,Haedrich, R., Montagna, P., Baguley, J., Berhard, J., Wickerson, M., Ammons, A., Briones, E., Solimna, Y., and Deming, J., 2008. Comparative biomass structure and estimated carbon flow in food webs in the deep Gulf of Mexico. Deep-Sea Research II, 55: 2699-2711.

Stepnowski, P. and Skwarzec, B., 2000. A comparison of $^{210}Po$ accumulation in molluscs from the southern Baltic, the coast of Spitzbergen and Sasek Wielki Lake in Poland Journal of Environmental Radioactivity, 49: 201-208.

Stewart, G., Cochran, J., Xue, J., Lee, C., Wakeham, S., Armstrong, R., Masque, P., and Miquel, J., 2007. Exploring the connection between $^{210}Po$ and organic matter in the northwestern Mediterranean. Deep-Sea Research Part 1, 54: 415-427.

Stewart, G.M. and Fisher, N.S., 2003. Bioaccumulation of polonium-210 in marine copepods. Limnology and Oceanography, 48(5): 2011-2019.

Stewart, G.M. and Fisher, N.S., 2003. Experimental studies on the accumulation of polonium-210 by marine phytoplankton Limnology and Oceanography, 48(3): 1193-1201.

Stewart, G.M., Moran, S.B. and Lomas, M.W., 2010. Seasonal POC fluxes at BATS estimated from $^{210}Po$ deficits. Deep-Sea Research Part 1, 57: 113-124.

Swarzenski, P.W., McKee, B.A., Sorensen, K. and Todd, J.F., 1999. $^{210}Pb$ and $^{210}Po$, manganese and iron cycling across the $O_2/H_2S$ interface of a permanently anoxic fjord: Framvaren, Norway. Marine Chemistry, 67: 199-217.

Talbot, R.W. and Andren, A.W., 1984. Seasonal Variations of $^{210}Po$ and $^{210}Pb$ concentrations in an oligotrophic lake. Geochimica et Cosmochimica Acta, 48: 2053-2063.

Theng, T.L. and Mohamed, C.A.R., 2005. Activities of $^{210}Po$ and $^{210}Pb$ in the water column at Kuala Selangor, Malaysia. Journal of Environmental Radioactivity, 80: 273-286.

Turner, R.E., Rabalais, N.N., Swenson, E.M., Kasprzak, M. and Romaire, T., 2002. Summer hypoxia in the northern Gulf of Mexico and its prediction from 1978 to 1995. Marine Environmental Research 59(1): 65-77.

Verdeny, E., Masque, P., Maiti, K., Garcia-Orellana, J., Bruanch, J.M., Mahaffey, C., and Benitez-Nelson, C.R., 2008. Particle export within cyclonic Hawaiian lee eddies derived from $^{210}$Po-$^{210}$Pb disequilibrium. Deep-Sea Research II, 55: 1461-1472.

# THE VITA

Patrick Robert Jones was born the son of Celeste Jones and Jeffrey Jones in Georgia. He grew up on St. Simons Island, Georgia with his brother, Logan Jones, and sister, Caroline Jones and graduated from Glynn Academy High School in 2007. He attended The College of Charleston in Charleston, South Carolina and graduated with a Bachelor of Science in Geology and Environmental Geoscience with a concentration in Environmental Science in 2011. While an undergraduate, Patrick was a member of the College of Charleston varsity swimming and diving team for four years and was named captain of the team his senior year. In 2011, he began graduate studies with Dr. Kanchan Maiti in the Department of Oceanography and Coastal Sciences at Louisiana State University. His master's research was a study on 210-Polonium dynamics in the northern Gulf of Mexico. Patrick defended his thesis on December 11, 2013.